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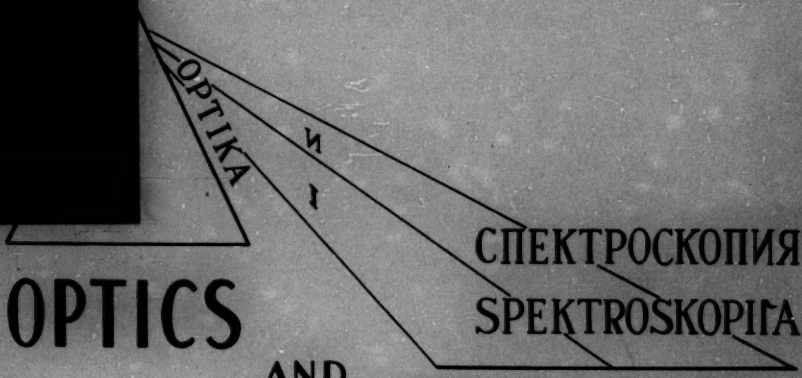

OPTICS AND SPECTROSCOPY

SPEKTROSKOPIIA

JUNE 1959 - VOL. VI - NO. 6
IIUN' 1959 - TOM. VI - VYP. 6

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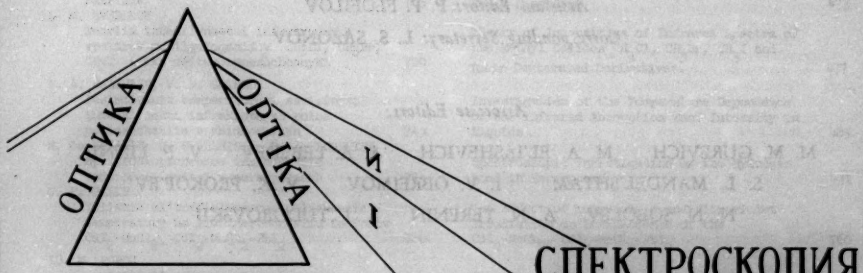

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Polarization of Luminescence of Helium Atoms Upon Excitation by Electron Impact

G. G. DOLGOV

Abstract: The polarization of the emitted radiation has been measured for four helium lines λ = 5016, 4921, 4471, and 3889 Å. The polarization has a non-monotonic dependence on the energy of the impinging electrons. The maximum polarization occurs 5-10 eV from the threshold. An explanation of the observed effect is given on the basis of a semi-classical model.

INTRODUCTION

The luminescence coming from atoms excited by a directed beam of electrons is partially polarized. The magnitude of the polarization and its dependence on velocity have been investigated for various atoms in a series of papers [1-3]. The most careful measurements of the polarization of the luminescence were made by Skinner and Appleyard [1] for the case of excited mercury atoms. It was shown that the polarization depends in a non-monotonic fashion on the velocity of impinging electrons, reaching a maximum at 3-4 eV. from the excitation threshold.

In reference [4] an explanation of this effect was given on the basis of a theory which used the Born first approximation. However the experimental results disagreed with this theory both quantitatively and qualitatively; the theory gave a monotonic dependence of the polarization on the energy of the impinging electrons.

The same author made an attempt to go beyond the limit of the Born approximation. In reference [5] he considered the relative probability of excitation of the S and P atomic levels near the excitation threshold. However, it is not this quantity which is important for polarization, but rather the relative magnitude of the probability of excitation of the magnetic sublevels of the atom under consideration. Reference [6] treated the polarization of the luminescence of mercury atoms on the basis of Born's first approximation, taking account of spin orbit interaction. The results of this work disagreed completely with experiment, however, giving a polarization of the wrong sign. The reasons for this divergence were not explained.

Despite the fact that the question under consideration has considerable importance for the theory of the collision of atoms with slow electrons, there has been no recent work published on either experiment or theory related to this problem. We therefore considered it useful to undertake an experimental and theoretical investigation of the simplest case. We chose helium as the object of our investigation.

DESCRIPTION OF THE APPARATUS

To obtain an electron beam of given energy, an electron-optical system similar to the one described in reference [7] was used, with an additional electrode placed between the anode and the focusing electrode of the electron gun. The introduction of this additional electrode assured the production of a highly parallel electron beam. The focusing electrode was a small metal box whose inside surface was covered with colloidal graphite. Observation of the luminescence took place through diametrically opposite cuts in the focusing electrode. The electron gun was placed in a vacuum system which was evacuated to a pressure of 2.10^{-6} mm. Hg. At this pressure the luminescence of the remaining gas could not be observed. Helium was then introduced into the system through a needle valve. During the experiment, the helium pressure in the system was maintained at 2.10^{-4} mm. Hg and was monitored with an ionization manometer. The current density of the beam was $5\mu A/mm.^2$ The average scatter of electron energies was from 0.5 to 0.7eV.

By definition, the polarization P of the radiation is determined by the relation

$$P = \frac{J_{\parallel} - J_{\perp}}{J_{\parallel} + J_{\perp}}, \tag{1}$$

where $J_{\parallel}$ is the component of the light intensity polarized parallel to the electron beam and $J_{\perp}$ is the component polarized perpendicular to the electron beam.

For direct measurement of the above ratio the following apparatus was used. Light from the excitation source was passed through a modulator, whose construction is shown in figure 1. The center of the modulator contained a piece of polaroid. The peripheral part had two sectors cut out (arranged 180° apart); the angular aperture of each sector was 90°. When the movable section of the modulator is rotated (figure 1, a.) the variable component of the light intensity travelling through the central part of the modulator is proportional to $|J_{\parallel} - J_{\perp}|$ whereas the component of the intensity going through the peripheral section is proportional to $|J_{\parallel} + J_{\perp}|$, i. e. to the total source intensity. The modulator was rotated at 438 rpm by a SD-09 synchronous motor, In order to exclude the polarization due to the spectral apparatus itself, a $\lambda/4$ plate was placed at the rear of the modulator and was rotated with it. By this means the polarization contributed by the spectrograph was completely excluded.

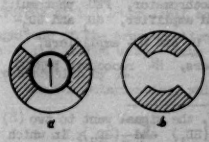

Figure 1. The polaroid modulator.

a. the moving part of the modulator, containing the polaroid,

b. peripheral section of the modulator.

After traversing the modulator, the light fell on monochromator M (figure 2), which isolated the desired spectral line. After this, the light fell on a FEU photomultiplier. The electric signal

from the multiplier was amplified by a narrow band amplifier (US). After leaving the amplifier the signal had the form

$$(2) \quad A=(J_{\parallel}+J_{\perp})\cos 2\omega t + (J_{\parallel} - J_{\perp})\cos(2\omega t + \alpha),$$

where ω is the angular velocity of the modulator, α is the difference in phase between the signal through the polaroid and the signal through the peripheral part of the modulator. In our case the phase shift was kept equal to 90°.

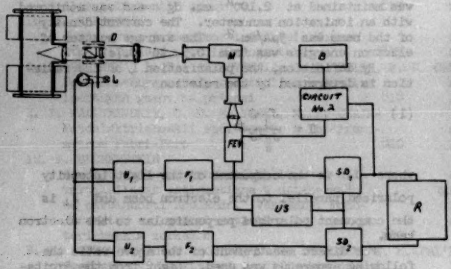

Figure 2. Block diagram of the apparatus O- modulator, M- monochromator, FEU- photomultiplier, US- narrow band amplifier, SD_1 and SD_2- synchronous detectors, U_1 and U_2- amplifiers, F_1 and F_2- phase shifters, R- rheochord ERR-09, L- lamp, B- battery.

From the amplifier, the signal went to two synchronous detectors (SD_1) and (SD_2), in which the switching voltages were displaced 90° with respect to each other with the help of the phase-shifters (F_1) and (F_2). With the help of the circuit described in reference [8], the signal from the first detector SD_1 (proportional to $J_{\parallel} + J_{\perp}$), was kept constant and fed into a EPP-09 rheochord, whereas the signal from the second detector was put on the slide of the rheochord. By varying the voltage on the focusing electrode of the electron gun, we obtained a direct record of the dependence of the magnitude of luminescence polarization on the energy of the impinging electrons.

The minimum polarization which could be measured with this apparatus was 2%.

RESULTS OF THE MEASUREMENTS

In figure 3 we give curves of the polarization of the luminescence as a function of the energy of the impinging electrons for the following helium lines:

$\lambda_1$5016 Å $(2^1S - 3^1P)$,
$\lambda_2$4921 Å $(2^1P - 4^1D)$,
$\lambda_3$3889 Å $(2^3S - 3^3P)$,
$\lambda_4$4471 Å $(2^3P - 4^3D)$.

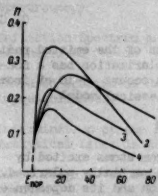

Figure 3. Dependence of polarization on energy of the incident electrons. Wavelengths (in Å): 1- 5016 (2^1S-3^1P), 2- 4921 (2^1P-4^1D), 3- 4471 (2^3P-4^3D), 4- 3889 (2^3S-3^3P). $E_{пор.} = E_{thr.}$ (excitation threshold).

As expected, the polarization of the luminescence is equal to 0 for a helium line whose upper level is either ^1S or ^3S. The 13% figure found for the polarization of the helium line $2^1P - 3^1S$ (λ = 5047Å) given in reference [2] is apparently an error.

Near the excitation threshold, the polarization curves rise steeply, and reach a considerable magnitude at a distance of the order of 0.5 eV from the excitation threshold. We list below the polarization values for the four helium lines at a distance ΔE = 0.5 eV from the excitation threshold:

λ (in Å)	5016	4921	4471	3889
η	0.08	0.12	0.08	0.05

Unfortunately we did not succeed in obtaining a sufficiently monochromatic electron beam to measure the value of the polarization for $\Delta E < 0.5$eV. Such measurements would obviously be of great interest.

DISCUSSION OF RESULTS

As has already been pointed out, there is not only quantitative but also qualitative disagreement between the observed experimental dependence of polarization on the energy of the impinging electrons and the theoretical calculations made on the basis of Born's first approximation. It has been shown [9] that the use of a more accurate method of calculation in place of the Born approximation does not lead to qualitative agreement with experiment. As may be seen from figure 3, the polarization near the threshold goes to (or close to) zero, and at higher electron energies reaches a maximum at a distance of several electron volts from the excitation threshold. On the other hand the theoretical curves have a monotonic form, reaching their greatest value at an energy of the incident electrons equal to the excitation energy of the level being observed. This difference cannot be explained by experimental errors in the measurements.

In our case errors could be due to two factors. First, the non-monochromaticity of the electrons, and second, the occurrence of transitions from higher levels to the level under consideration. As may be shown, both of these factors lead to a decrease in the observed value of the polarization. In the first case, an imperfectly monochromatized electron beam cannot give additional maxima but can only smooth out somewhat the observed dependence of the polarization on energy.

At energies exceeding the threshold energy by several electron volts, direct as well as cascade

transitions from upper levels to the level under consideration begin to play a role. But since the excitation cross-section of atomic levels decreases with increasing principal quantum number [10], the influence of transitions from upper levels on polarization is comparatively small. One can show that in this case the polarization is given by the expression

$$\Pi = \frac{\Pi_0}{1 + \dfrac{\sum_k \sigma_k A_{k1}}{\sigma_1 A_{10}}} \qquad (3)$$

where Π_0 is the degree of polarization ignoring cascade transitions, σ_k is the excitation cross-section of the k^{th} level, A_{k1} is the probability of a transition from the k^{th} level to the level under consideration, σ_1 is the excitation cross-section of the level being observed, and A_{10} is the probability of a transition from the level under consideration to the initial level.

In addition we measured the excitation functions of helium (cf. fig. 4). The form of excitation functions coincides basically with those given in reference [11]. The contribution to the excitation cross-section from the various levels involved in effects related to cascade transitions is, it would seem, 10-15 %. Thus the divergence of the observed form of the polarization curve from the theoretical curve of the dependence on energy of the incident particles cannot be explained by the presence of cascade transitions.

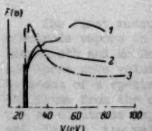

Figure 4. Excitation functions for the various helium lines. Wavelengths (in Å): 1- 5016 (2^1S-3^1P), 2- 4921 (2^1P-4^1D), 3- 4471 (2^3P-4^3D), 4- 3889 (2^3S-3^3P).

We now consider a quasi-classical picture of the excitation of an atom by a charged particle. (For simplicity we will consider only the S-P transitions of the atom.) During the time that the charged particle flies by at a distance given by the collision parameter ρ, a field is applied which induces a transition in the atom from an S to a P state. The dependence of the field on time is given by the expression $V(t) = 1/|\vec{R}(t) - \vec{r}|$, where $\vec{r}$ is the position of the atomic electron, $\vec{R}(t)$ is the position of the impinging electron. The transition probability is determined by the square of the absolute value of the matrix element

$$|a|^2 = \left| \int_{\vec{r}} \int_{-\infty}^{+\infty} \psi_1^* V(t) \psi_0 e^{i\omega_{SP} t} \, dt d\vec{r} \right|^2 . \qquad (4)$$

Assuming that the axis of quantization points along the wave vector of the incident particle, and limiting ourselves to the dipole approximation

$$V(t) = \frac{\vec{R}(t)\vec{r}}{R^3(t)} ,$$

we find

$$|a|^2 = |a_0|^2 + |a_{\pm 1}|^2 \qquad (5)$$

$$|a_0|^2 = |A_0|^2 \frac{\omega^2}{v^4} K_0^2\left(\frac{\rho}{v}\omega\right);$$

$$|a_{\pm 1}|^2 = |A_{\pm 1}|^2 \frac{\omega^2}{v^4} K_1^2\left(\frac{\rho}{v}\omega\right),$$

where $|a_0|^2$ and $|a_{\pm 1}|^2$ are the excitation probabilities of the sublevels with $m = 0$ and $m = \pm 1$ respectively, and where

$$A_0 = \langle 0|z|1\rangle , \qquad (6)$$

$$A_{\pm 1} = \langle 0|x \pm iy|1\rangle .$$

The total excitation cross-section for a given velocity, equal to

$$\sigma_i = 2\pi \int_{\rho_0}^{\infty} |a_i|^2 \rho d\rho , \qquad (7)$$

diverges at the lower limit as $\rho_0 \to 0$. However, the magnitude of the cross-section depends only slightly on ρ_0: a change of ρ_0 from 0.1 to 1 changes the cross-section by 5%.

For the polarization, which is by definition

$$\Pi = \frac{\sigma_0 - \sigma_{\pm 1}}{\sigma_0 + \sigma_{\pm 1}} , \qquad (8)$$

we find

$$\Pi = \alpha \left\{ \frac{K_1(\alpha)}{K_0(\alpha)} - \frac{K_2(\alpha) + K_1(\alpha)}{K_1(\alpha)} \right\} , \qquad (9)$$

where

$$\alpha = \frac{\rho_0 \omega}{v} .$$

In figure 5 we show the theoretical dependence of polarization on the velocity of the impinging particles as calculated from (9). As is obvious

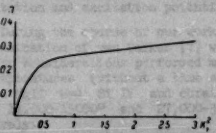

Figure 5. Polarization as calculated from formula (9).

from figure 5, this formula agrees qualitatively with the observed curves, giving an increase in polarization with increasing velocity of the incident particles.

The above calculations, of course, are not strictly applicable to the scattering of electrons. However, one may state that the qualitative character of the dependence of the polarization on the velocity would be the same even in a rigorous treatment of the present problem. In support of this proposition one may observe that during collision with heavy particles, the experimental dependence of the polarization on energy has the same form, and the above calculations are more likely to be valid.

In conclusion the author thanks S. L. Mandel'shtam for his interest in the present work, and L. A. Kulevskii for carrying out the measurements.

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On the Temperature of Electrode Vapors in a Spark Discharge

N. K. SUKHODREV AND S. L. MANDEL'SHTAM

Abstract: The generally accepted value of $T \approx 10{,}000^\circ$ K for the vapors of electrodes in a spark must characterize only the peripheral cooler regions of the vapor cloud; this value is the result of using only "low-temperature" spectral lines for measurement.

Results are cited from measurements on lines of Al III, Sn IV and Si IV giving values of $T \approx 30 - 35{,}000^\circ$. This value apparently characterizes the central portions of the vapor clouds. It is close to the value of the temperature of the canal $\approx 30{,}000 - 40{,}000^\circ$ C, which confirms the assumption that the heating and excitation of the electrode vapors occurs during their passage through the spark canal.

INTRODUCTION

Electrode vapors in a spark enter into the discharge space, as is well known, like flames or torches. Deliberations set forth earlier [1], permit us to assume that the distribution of atoms in the ionized phase and in excited states is accounted for by formulas of Sachs and Boltzmann, with the electron temperature as a parameter; furthermore, in practice $T_e = T_g$, the temperature of the gas. In this manner, the spectra of atoms and ions of elements entering into the construction of the electrodes, are characterized in a spark discharge, by the temperature T of the vapors, and a knowledge of this temperature is of definite interest when using a spark as a source of spectral excitation during spectroscopic investigations and spectral analyses.

The measurement of the temperature of electrode vapors was repeated many times. In all cases the spectroscopic method of Ornstein was used, based on the measurement of the relative intensities of two or more lines of some element entering into the composition of the vapors; we employ the method assuming a Boltzmann distribution of atoms in the excited levels, and this gives the electron temperature T_e.

The first measurements of the temperature of electrode vapors in a spark were performed by Langstroth and Mc Rae on several pairs of Sn I lines, and these gave values of $T \approx 9{,}000^\circ$ [2]. Sobolev, by means of a special procedure, spatially isolated the flame from the canal and measured the temperature of electrode vapors from lines of Ri I, Fe I, and Fe II; the values of temperature obtained were $\approx 10{,}000^\circ$ at the beginning of the flame, decreasing to $\sim 5{,}000^\circ$ toward the end of the flame [3].

After this, there followed a whole series of experiments in which the temperature of the flame was measured under the most diverse conditions, among them being the development of the spectrum in time [4-8]. A very wide range of values of temperature was obtained from $5{,}000 - 20{,}000^\circ$,* and at the same time during this work, it was established that the temperature of a discharge, for the same element, has different values from measurements on arc and on spark lines, and similarly, from lines of different elements present simultaneously in the discharge. On this basis the deduction was made by a number of authors that, in a flame, there is no single excitation temperature.

As was pointed out in our previous report [9] the formation of directed streams of electrode vapors depended on a process similar to that of an explosion. The vapors, upon departing possess a comparatively low temperature and do not glow, but their excitation apparently occurs upon their passage through the region of the discharge canal. The temperature of the discharge canal is $30\text{-}40{,}000^\circ$, and consequently it can be expected that the maximum temperature of the electrode vapors is near this value. Therefore, the experimental values of temperature $\sim 10{,}000^\circ$, observed in the majority of works apparently characterize the colder peripheral sections of the vapor clouds. This is explained by the fact that in all these works, there were selected for measurements "low-temperature" lines ** which have appreciable intensities only at temperatures of $\sim 5{,}000 - 10{,}000^\circ$, and which are not able to characterize even the effective temperature, much less the maximum temperature of the cloud [6,9-11]. In order to be able to measure the maximum heating temperature of the vapors, it is essential to use atomic lines belonging to high degrees of ionization.***

We have mentioned the possibility of using for such measurements lines of doubly- and triply-ionized atoms of Al, Ag, Ba, Cu, Ca, Mg, Pb, Sn, Si, Zn. The most appropriate turned out to be the lines listed in Table 1. The transition probabilities for these lines were evaluated on the basis of a single-electron approximation with the aid of tables by Bates and Damgaard [12]. In Table 1 are also listed the characteristics of N II lines which were used for the determination of the temperature of the canal.

EXPERIMENTAL SECTION

Measurements were carried out with time resolution, partly with an ISP-51 glass optics

*Cundall and Craggs [8], using arc lines, obtained temperatures approaching $90{,}000^\circ$, However, they used Mg I lines terminating in a metastable level. We photographed the spectrum of a spark under conditions near those of [8] and discovered that these lines can be strongly self-reversed and are not appropriate for temperature measurements. Cundall and Craggs conducted measurements by a photoelectric method and did not include line self-reversal.

** By "low temperature" lines we understand them to be those belonging to atoms or ions with low ionization and excitation potentials.

*** During the course of our work there appeared the communication of van Calker [7] who on the basis of similar considerations performed measurements of vapor temperatures (without a time scan) on lines of MgI, MgII and Si IV and obtained values of $6{,}000^\circ$, $11{,}000\text{-}15000^\circ$ and $27{,}000\text{-}33{,}000^\circ$, respectively.

Table 1

Element	Wave-Length (in Å)	Transitions	Transition Probability (Ag.10^{-8} sec.$^{-1}$)	Energy of Upper Level E, in eV.
N II	3919,00	$3p^3P_1 - 3d^3P^0_0$	2.94	23.47
	3994,996	$3s^1P^0_1 - 3p^1D_2$	7.51	21.51
	5535,30	$3s^3P_{1,2} - 3p^3D^0_{1,2}$	6.30	27.61
	5496,70	$3p^3P_2 - 3d^3P^0_1$	1.54	23.31
	5045,088	$3s^3P^0_2 - 3p^3S_1$	1.29	20.85
Al III	5696,47	$4^2S_{1/2} - 4^2P^0_{3/2}$	3.4	17.74
	5722,65	$4^2S_{1/2} - 4^2P^0_{1/2}$	1.7	17.73
	4529,18	$4^2P^0_{3/2} - 4^2D_{3/2,5/2}$	16.3	20.47
	4512,54	$4^2P^0_{1/2} - 4^2D_{3/2}$	8.2	20.47
Sn IV	2948,51	$6^2P^0_{3/2} - 6^2D_{5/2}$	39.8	29.8
	2887,79	$5^2D_{3/2} - 6^2P^0_{1/2}$	11.8	24.5
Si IV	4116,10	$4^2S_{1/2} - 4^2P^0_{3/2}$	3.0	26.95
	4088,86	$4^2S_{1/2} - 4^2P_{1/2}$	6.0	26.97
	3165,72	$4^2P^0_{3/2} - 4^2D_{5/2,3/2}$	31.8	30.86
	3149,56	$4^2P^0_{1/2} - 4^2D_{3/2}$	15.8	30.86

spectrograph (camera f = 270 mm), and party with an ISP-22 quartz spectrograph.

The diagram of the principle of the apparatus is shown in figure 1:

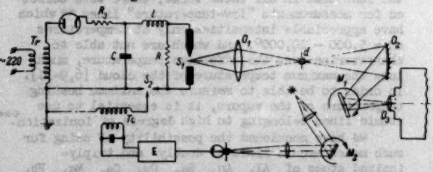

Figure 1 Optical and electrical scheme of the apparatus. (Mirrors M_1 and M_2 are on the same axis).

A portion of the spark S_1, formed between vertical electrodes, was imaged (by the objective O_1) in the plane of the intermediate slit (d = 0.4 mm), and then was focused on the spectrograph slit by the concave mirror O_2 and rotating mirror M_1. Upon rotation of the mirror M_1, the image of the isolated portion of the spark moved along the slit, and on the photographic plate there resulted a time development of the discharge spectrum. The presence of the antivignetting lens O_3, imaging the revolving mirror M_1 in the plane of the camera objective, guaranteed use of the same portion of the optical system of the spectrograph upon motion of the source image along the slit. The rate of scan on the photographic plate could be changed from 1 to 3 mm/msec, with a resulting time resolution of from ~ 0.4 to 0.1 μsec, respectively.

To synchronize the moment of ignition of the spark with the position of the rotating mirror, a photoelectric data unit was used, the signal from which, transformed in a suitable manner by means of a special electron circuit E, was fed to the firing electrode of the three-way air gap, S_2. The ignition of the spark occurred at the moment when the image of the spark S_1 coincided with the beginning of the operating portion of the spectrograph slit. The spread of the repeated impulses during the ignition time did not exceed 0.5 μsec. The parameters of the spark contour S_1 are: C = 0.01, 0.125, 1 mf; L = 2, 25, 280, 1000, 3000 μH; the voltage at the gap V = 15 kV; the distance between electrodes was 2.5 mm.

The characteristic form of the spectral development of the spark between tin electrodes is shown in figure 2. On the print are visible the clearly defined oscillations of the intensity of lines belonging to ions Sn IV, N II and O II, characteristic of current fluctuations. This attests to the fact that lines of Sn IV are definitely excited in the spark canal. However, lines of Sn I do not show such oscillations and their radiation emanates from the colder cloud of the surrounding vapors.

Figure 2. Mirror development of a spark spectrum between tin electrodes.
C = 0.125 mf; L = 25 μH; V = 15 kV.

Measurements on Sn IV lines were performed on a set-up for ultraviolet region of the spectrum. The two lines used are sufficiently close to each other so that one may disregard the differences of spectral sensitivity of the plates and the transmittance of the optical system. Curves of blackening were constructed with the aid of a step-attenuator for one of the Sn lines in the discharge (the mirror for this experiment was stationary). In the portion of tests when both electrodes were of metallic tin, the intermediate diaphragm removed all but the central portion of the discharge. In other tests there was used a copper or tungsten counter-electrode, which gave the opportunity of ascertaining the influence of electrode polarity on the temperature of the vapors; the intermediate diaphragm in this case removed all but the region near the tin electrode. In a number of tests a simultaneous measurement of the vapor temperatures was made from Sn IV lines and the temperature of the spark canal from N II lines.

Measurements of temperature using Al III lines were made on a set-up for the visible region of the spectrum. Since these lines differ greatly in their wavelengths, the method of heterochromatic photometry was used. The continuous spectrum of a ribbon filament lamp of known color temperature served as a comparison source. The characteristic curves were obtained with the aid of a 9-step platinum attenuator. To eliminate the Schwartzhield effect, the photographing of the lamp spectrum was made with the mirror revolving at the same rate as used for scanning of the spark spectrum. Since the lines used possess considerable width, the contour

of the line was plotted and then integrated graphically. The ratio of line intensities in the multiplet was found to be 2:1, showing that the criterion of no noticeable reabsorption was fulfilled. In cases when reabsorption began to appear, in place of an aluminum electrode an electrode of bronze with ~ 10% Al content was used. A copper or tungsten electrode served as the other electrode. In a portion of the tests the temperature of the canal was measured using N II lines.

The measurement of flame temperatures using Si IV lines was performed on a set-up for the ultraviolet region of the spectrum. In these experiments the electrodes were prepared of silumin with ~ 10% silicon content. In view of the low intensities of the lines, these measurements were carried out without time scanning the spectrum, i.e. a time integrated line intensity was determined; as a source of spectrum excitation a spark generator, IG-2, was used. The Si IV lines are also situated far from one another, which demands the application of heterochromatic photometry. As a source of comparison with a known distribution of spectral intensity in the ultraviolet region, a standard direct current arc between iron electrodes was used, for which measurements of Crosswhite [13] exist. It should be pointed out that in the vicinity of the Si IV lines, $\lambda = 4088/4116$ Å, there exists a very strong background so that the accuracy of these measurements is not great.

MEASUREMENT RESULTS

The results of measurements of temperature using Sn IV lines are shown in Tables 2 - 4.

Table 2 refers to the case when both electrodes are of tin.

Table 2

Time (microsec)	Temperature, °K: 0.125 mf, 25 μh	1 mf, 25 μh	1 mf, 300 μh
1.5	27000	—	—
4	27000	28000	—
7	27000	28000	—
10	28000	28000	25000
13	29000	29000	26000
16	28000	30000	26000
19	29000	30000	26000
22	—	30000	25000
25	—	31000	25000
28	—	—	26000

In Table 3 are shown results of measurements with a copper counter-electrode; the measurements refer to the moment corresponding to the current maximum in each half-cycle of the discharge.

In Table 4 are shown the results of simultaneous measurements of temperature using Sn IV lines and lines of N II, $\lambda = 3919.0$ Å and $\lambda = 3994.99$ Å.

The results of measurements of temperature using Al III lines are shown in Table 5. The measurements refer to the instant of time corresponding to the current maximum in the first half-cycle of the discharge.

Table 3

C = 0.125 mf; L = 25 μh

Time (microsec)	Film No. 1: Polarity of Sn Electrode	Film No. 1: T°K	Film No. 2: Polarity of Sn Electrode	Film No. 2: T°K
3	Cathode	—	Anode	31000
8	Anode	27000	Cathode	29500
14	Cathode	27000	Anode	27000

Table 4

C = 1 mf; L = 25 μh

Time (microsec)	Temperature from lines of Sn IV	Temperature from lines of N II
1.5	26000	38000
7	27000	34000
16	26000	35000
22	27000	31000

The measurement of temperature by Si IV lines was carried out only for one set of electrical circuit parameters and gave an extremely large scatter of values; the results are shown in Table 6.

A study of the results obtained shows that measurements using Sn IV lines give a temperature lying in the vicinity of 28,000°, measurements with Al III lines in the vicinity of 30,000° and with Si IV lines in the vicinity of 35,000°. The scatter in the results, however, is of such magnitude that it is difficult to state whether this difference in temperature is real, even though, taking account of the methods employed, one might expect a small difference in temperatures for the following series of values: Al III, Sn IV; Si IV. Disregarding the changes in the parameters of the spark circuit over wide limits, the scatter of the results does not permit the detection of the possibly existing dependence of temperature on the discharge parameters.

It should be kept in mind that in the region of high temperatures, measurements using the method of Ornstein are very inaccurate. In fact, it is easy to see that

$$\Delta T = \frac{0.43T^2}{5040 \cdot \Delta E}\left|\frac{\Delta R}{R}\right|,$$

where $R = \frac{I_1}{I_2}$ is the relative intensity of the measured lines. In view of the strong background, the error in measurement of $\left|\frac{\Delta R}{R}\right|$ may approach 10%, which, with $T \approx 30{,}000°$ and $\Delta E \approx 4$ eV, gives a $\Delta T \approx 2{,}000°$. In a similar manner, examining the error which an error in the values of the relative

Table 5

POLARITY	Temperature									
	C = 0.02 mf L ≈ 2 μh (generator IG-2)		C = 0.01 mf L ≈ 2 μh		C = 1 mf L = 25 μh R = 6 ohms		C = 1 mf L = 280 μh		C= 1 mf L ≈ μh	C=0.125 mf L≈3000 μh
	Lines Al III	Lines N II	Lines Al III	Lines N II	Lines Al III	Lines N II	Lines Al III	Lines N II	Lines Al III	Lines Al III
Cathode	40000	37000	31000	37000	31000	35000	27000	40000	–	19000
Anode			–	–	–	–	26000	36000	29000	–

Table 6

C = 0.02 mf; L ≈ 2 μh (IG-2)

Number of Photo-Graph	1	2	3	4	5	6	7	8
T°K	47000	32000	32000	25000	36000	23000	38000	44000

$T^{\circ}_{av.} = 35000^{\circ}$

transition probabilities introduces into a determination of the temperature, we obtain

$$\Delta T = \frac{0.43T^2}{5040 \cdot \Delta E} \left|\frac{\Delta K}{K}\right|,$$

where $K = \frac{A_1}{A_2}$. For the approximate methods of calculation used the magnitude $\left|\frac{\Delta K}{K}\right|$ may approach 20%, which gives $\Delta T \approx 4{,}000^{\circ}$.

Therefore, the above mentioned value of vapor temperature in a spark, $T \approx 30{,}000 - 35{,}000^{\circ}$, should be looked upon as an approximation. We note that it does agree well with calculated values. In figure 3 are shown the intensities of lines employed, as functions of temperature, evaluated according to formulas of Sachs and Boltzmann (for $N_e \approx 10^{17}$ cm^{-3}). It follows from the curves that the excitation of these lines actually does occur in the interval of temperature of 30,000 - 45,000° *.

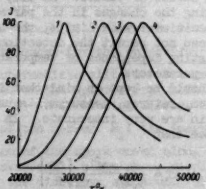

Figure 3. Calculated dependence of intensity on temperature.

1 - Al III (λ=5696 Å); 2 - N II (λ=5495 Å); 3 - Sn IV (λ=2887 Å); 4 - Si IV (λ=4088 Å). (Intensity of lines at the peak normalized to 100).

*A change of the N_e within the limits of 3×10^{16} to 3×10^{17} shifts the position of the maxima by approximately 3,000 - 5,000°.

A temperature of ≈ 35,000° corresponds to the temperature of the spark canal, determined from lines N II and N III earlier [1], and in this paper. This confirms the hypothesis that the luminescence of the electrode vapors in a spark discharge results from their being heated in the canal, and the temperature of the vapors approaches the temperature of the canal.

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Theory of Intensities of Infrared Spectra of the Methyl Halides CH_3Cl, CH_3Br, CH_3I and Their Deuterated Derivatives

L. M. SVERDLOV

A calculation was made of intensities of infrared bands and electro-optical parameters of methyl halide molecules CH_3Cl, CD_3Cl, CH_3Br, CD_3Br, CH_3I and CD_3I in a first approximation valence-optical scheme. Good agreement was obtained between calculated and found intensities. It was shown that the negative end of the dipole μ_{CH} is found on the carbon atom, while the positive end is on the hydrogen atom. On increasing the length of the C-H and C-Z bonds the dipole moments are made smaller.

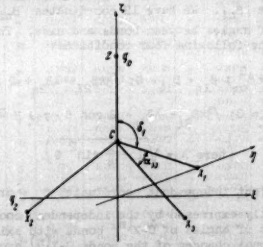
1. In the last few years much work has been published on measurements of the absolute integral intensities of the infrared absorption spectra of various molecules. Using the data obtained authors carried out calculations of electro-optical parameters (dipole moments of the bonds μ and derived dipole moments according to the change of the bond length $\partial\vec{\mu}/\partial q$) of molecules in a zero approximation valence-optical scheme, formulated first by Vol'kenshtein [1], and in subsequent development by Vol'kenshtein and El'iashevich [2]. However, under these circumstances, in the overwhelming majority of cases, results were obtained which have no physical significance, since μ and $\partial\mu/\partial q$, which were calculated on the basis of intensities of bands corresponding to vibrations of different types of symmetry, have unequal meaning, i.e. for each type of symmetry their own values of the electro-optical parameters of the separate bonds were used.

Meanwhile it is evident that in all vibrations the values μ and $\partial\mu/\partial q$ ought to remain unchanged, since they are determined by the structure of the electronic shell, and are the same characteristic constants of the electronic shell of the molecule as, for example force coefficients of interatomic spacings.

The difficulties indicated might be explained either by the irreconcilabilty of the valence-optical scheme in the zero approximation and the necessity of using higher approximations, or by the irreconcilability of the semiclassical theory of intensities (the valence-optical scheme) and the necessity of using quantum-mechanical methods. In order to elucidate which of these suppositions is correct it is necessary to carry out calculations of intensities of infrared spectra in the first approximation of the valence-optical scheme, drawing in for this purpose all the experimental material available. Earlier [3] we carried out similar calculations of the intensities of infrared bands of ethylene and tetradeuteroethylene, which actually showed that it is necessary to use the first approximation of the valence-optical scheme for calculating intensities. It was of interest to check this conclusion not only with an example of compounds with a double bond, containing π-electrons, but also with other classes of compounds. Carrying out similar calculations permits us to obtain important parameters which are characteristic of the distribution of the electron cloud in the molecules and the polarity of the different bonds.

In this paper a calculation is made of the intensities of infrared bands and electro-optical parameters of methyl chloride, bromide, iodide and their deuterated derivatives in a first approximation of the valence-optical scheme.

2. Intensities of the infrared absorption spectra of methyl halides were investigated repeatedly. The first measurements of the absolute integral intensities of the infrared bands of methyl halides was carried out by Barrow and MacKean [4]. The most trustworthy results were obtained in a recently published work by Dickson, Mills and Crawford [5] in which, with high precision, measurements were made of the absolute integral intensities of the infrared bands of the molecules CH_3Cl and CD_3Cl, CH_3Br and CD_3Br, CH_3I and CD_3I. Using their results the authors of papers [4 and 5] calculated the electro-optical parameters μ and $\partial\mu/\partial q$ of the indicated molecules in the zero order approximation of the valence-optical scheme, and obtained unequal values of the parameters μ_{CH} and $\partial\mu_{CH}/\partial q$ for different types of symmetry, which is devoid of physical meaning.



3. The methods of Vol'kenshtein and El'iashevich [1,2,6] were used as the basis for carrying out the computation. In the monograph [6] are presented expressions for derivatives of the dipole moment for normal coordinates $\partial P/\partial Q$ of molecules of the type CX_3Z (which possess tetrahedral angles) in the zero approximation of the valence-optical scheme. However, as experiment shows [7], the angles in molecules of methyl halides diverge from tetrahedral, so it is necessary to examine the general case of CX_3Z molecules with non-tetrahedral angles.

For the calculation we will introduce the natural vibrational coordinates of a change in the length of the bonds and the values of the angles: q_0, q_1, δ_1 ($i=1,2,3$), α_{12}, α_{13}, α_{23} (see figure). Of the 10 coordinates 9 are independent, for the angular coordinates are connected by the condition

$$(\alpha_{12}+\alpha_{13}+\alpha_{23})\kappa + \cos\theta\,\lambda\sqrt{3}\,(\delta_1+\delta_2+\delta_3)=0. \quad (1)$$

where θ is the supplementary angle to $\theta_1 = \angle XCZ$; $\kappa = \cos\frac{\theta_2}{2}$ ($\theta_2 = \angle XCX$). The molecule CX_3Z belongs to symmetry group C_{3v} and has three fully symmetrical vibrations of type A_1 and three doubly degenerate vibrations of type E. We have the following coordinates of symmetry $S_k^{(\kappa)}$:

$$q_o^{A_1};\ q^{A_1} = \frac{1}{\sqrt{3}}(q_1 + q_2 + q_3);\ \alpha^{A_1} = \frac{1}{\sqrt{3}}(\alpha_{12} + \alpha_{13} + \alpha_{23});$$

$$\delta^{A_1} = \frac{1}{\sqrt{3}}(\delta_1 + \delta_2 + \delta_3);\ q^{EII} = \sqrt{\frac{2}{3}}\left(q_1 - \frac{1}{2}q_2 - \frac{1}{2}q_3\right);$$

$$\alpha^{EII} = \sqrt{\frac{2}{3}}\left(\alpha_{23} - \frac{1}{2}\alpha_{12} - \frac{1}{2}\alpha_{13}\right);\ \delta^{EII} = \sqrt{\frac{2}{3}}\left(\delta_1 - \frac{1}{2}\delta_2 - \frac{1}{2}\delta_3\right).$$

Coordinates of symmetry of the following kind are expressed through the normal coordinates q_l ($S_k^{(\kappa)} = \sum_l L_{kl} q_l$):

$$q_o^{A_1} = \sum_{l=1}^{3} C_{o_l} q_l;\ q^{A_1} = \sum_{l=1}^{3} C_{ql} q_l;\ \alpha^{A_1} = -\frac{\sqrt{3}}{\kappa}\cos\theta\,\delta^{A_1}$$

$$= \sum_{l=1}^{3} D_{\alpha l} q_l;\ q^{E} = \sum_{l=4}^{6} C_{ql} q_l;\ \alpha^{E} = \sum_{l=4}^{6} D_{\alpha l} q_l;\ \delta^{E} = \sum_{l=4}^{6} D_{\delta l} q_l.$$

We pass on now to the angular valence-optical coordinate β_{ni}. We have 12 coordinates β_{ni} the changes of angles between bonds and axes. They satisfy the following four conditions:

$$\beta_{o\zeta}^2 = \beta_{o\xi}^2 + \beta_{o\eta}^2;\ \beta_{1\eta} - \beta_{1\zeta} = 0;\ \sqrt{3}\kappa\beta_{2\xi} + \lambda\beta_{2\eta} + 2\cos\theta \cdot$$

$$(2)\quad \chi\,\beta_{2\zeta} = 0;\ \sqrt{3}\kappa\beta_{3\xi} - \lambda\beta_{3\eta} - 2\cos\theta \cdot \gamma_{3\zeta} = 0$$

$$\left(\text{here } \lambda = \sqrt{1 - \tfrac{1}{4}\sin^2\theta}\right).$$

Eight independent coordinates β_{ni} are conveniently expressed by the independent coordinates φ (changes of angles of $C\text{-}X^{(n)}$ bonds with axis ζ), ψ (rotational changes of the bonds $C\text{-}X^{(n)}$ around the axis ζ), and ω (rotation of the bond C-Z in the planes $\zeta\xi$ and $\zeta\eta$):

$$\beta_{o\xi} = -\omega_\xi;\ \beta_{o\eta} = -\omega_\eta;\ \beta_{o\zeta} = \sqrt{\omega_\xi^2 + \omega_\eta^2};\ \beta_{1\xi} = \sin\theta \cdot \psi_1;$$

$$\beta_{1\eta} = \varphi_1;\ \beta_{1\zeta} = \varphi_1;\ \beta_{2\xi} = -\frac{\sin\theta}{2\kappa}\psi_2 - \frac{\sqrt{3}}{2\kappa}\cos\theta \cdot \varphi_2;$$

$$(3)\quad \beta_{2\eta} = \frac{\sqrt{3}}{2\lambda}\sin\theta \cdot \psi_2 - \frac{\cos\theta}{2\lambda} \cdot \varphi_2;\ \beta_{2\zeta} = \varphi_2;$$

$$\beta_{3\xi} = -\frac{\sin\theta}{2\kappa}\psi_3 + \frac{\sqrt{3}}{2\kappa}\cos\theta \cdot \varphi_3;\ \beta_{3\eta} = -\frac{\sqrt{3}}{2\lambda}\sin\theta \cdot \psi_3$$

$$-\frac{\cos\theta}{2\lambda} \cdot \varphi_3;\ \beta_{3\zeta} = \varphi_3.$$

The valence-optical coordinates of symmetry have the form

$$\varphi^{A_1} = \frac{1}{\sqrt{3}}(\varphi_1 + \varphi_2 + \varphi_3);\ \varphi^{EII} = \sqrt{\frac{2}{3}}\left(\varphi_1 - \frac{1}{2}\varphi_2 - \frac{1}{2}\varphi_3\right);$$

$$\psi^{EII} = \frac{1}{\sqrt{2}}(\psi_2 - \psi_3);\ \omega^{EII} = \omega_\eta.$$

Expressing these by the normal coordinates we get

$$\varphi^{A_1} = \sum_{l=1}^{3} E_l q_l;\ \varphi^{EII} = \sum_{l=4}^{6} E_l q_l;\ \psi^{EII} = \sum_{l=4}^{6} F_l q_l;$$

$$\omega^{EII} = \sum_{l=4}^{6} G_l q_l.$$

Further, expressing the coefficients E, F and G by means of C and D, which are determined by solution of the mechanical problem:

$$(4)\qquad E_l^{A_1} = -\frac{\kappa}{\sqrt{3}\cos\theta} D_{\alpha l}^{A_1}\quad (l = 1,2,3),$$

$$(5)\qquad D_{\alpha l}^{EII} = \frac{\sqrt{3}}{2\kappa}\cos\theta \cdot E_l^{EII} - \frac{\sqrt{3}}{2\kappa} F_l^{EII}\quad (l = 4,5,6),$$

$$(6)\qquad \sqrt{\frac{2}{3}} D_{\delta l}^{EII} = \sqrt{\frac{2}{3}} E_l^{EII} - G_l^{EII}\quad (l = 4,5,6).$$

For vibrations of the type E II, besides (5) and (6), it is necessary to have one more condition, which we get by making the component of the moment of momentum with relation to the axis ξ equal to zero. It has the form

$$(7)\qquad cC_{ql}^{EII} + eE_l^{EII} + fF_l^{EII} + gG_l^{EII} = 0\quad (l = 4,5,6),$$

where *

$$(8)\quad \begin{cases} c = \left[\sqrt{\frac{3}{2}}\cos\theta \cdot \mu_b\rho_b - \frac{\sin\theta}{\sqrt{6}}\left(\mu_c\rho_c + \mu_d\rho_d\frac{3m_X}{m_C+3m_X}\right)\right], \\ e = \left[\sqrt{\frac{3}{2}}\sin\theta \cdot \mu_b\rho_b + \frac{\cos\theta}{\sqrt{6}}\left(\mu_c\rho_c + \mu_d\rho_d\frac{3m_X}{m_C+3m_X}\right)\right], \\ f = \left[\frac{1}{\sqrt{6}}\left(\mu_c\rho_c + \mu_d\rho_d \cdot \frac{3m_X}{m_C+3m_X}\right)\right];\ g = \frac{r_{CZ}}{r_{CH}}\mu_d\rho_d. \end{cases}$$

In these formulae the following designations were used:

$$\mu_b = \frac{2}{3}m_X;\ \mu_C = \frac{3m_X m_C}{m_C + 3m_X};\ \mu_d = \frac{m_Z(m_C+3m_X)}{m_Z+m_C+3m_X};$$

$$(9)$$

$$\rho_b = \frac{3}{2}r_{CH}\sin\theta;\ \rho_C = r_{CH}\cos\theta;$$

$$\rho_d = r_{CZ} + r_{CH}\cos\theta \ \chi\ \frac{3m_X}{m_C + 3m_X}$$

Further, as a result of unwieldy and complicated calculations, we obtain the following expressions

* In the corresponding formulae (22.31) and (22.36) of the monograph [6] (Vol. II) admitted errors (or misprints) were introduced for CX_3Z with tetrahedral angles.

for derivatives of the dipole moment in terms of the normal coordinate $\partial P_i / \partial Q_l$ in the first approximation:**

$$\frac{\partial P_\xi}{\partial Q_l^{A_1}} = \sum_k \frac{\partial P_\xi}{\partial S_k^{A_1}} L_{kl} = \left\{ \left[\frac{\partial \mu_{CZ}}{\partial q_o} - 3\cos\theta \cdot \frac{\partial \mu_{CH}}{\partial q_o} - 3\sin\theta \times \right.\right.$$

$$\times \mu_{CH} \frac{\partial \varphi_1}{\partial q_o} \Bigg] C_{ol}^{A_1} + \left[-\cos\theta \cdot \sqrt{3}\, \frac{\partial \mu_{CH}^{(1)}}{\partial q_1} - 2\cos\theta \cdot \sqrt{3}\, \frac{\partial \mu_{CH}^{(2)}}{\partial q_1} + \right.$$

$$\sqrt{3}\, \frac{\partial \mu_{CZ}}{\partial q_1} - \sin\theta \cdot \sqrt{3}\, \mu_{CH} \left(\frac{\partial \varphi_1}{\partial q_1} + 2\, \frac{\partial \varphi_2}{\partial q_1} \right) \Bigg] C_{ql}^{A_1} +$$

$$+ \left[-\sin\theta \cdot \sqrt{3}\, \frac{\mu_{CH}}{r_{CH}} - 2\cos\theta \sqrt{3}\, \frac{\partial \mu_{CH}^{(1)}}{\partial \varphi_1} \cdot \frac{1}{r_{CH}} \right.$$

$$\left.\left. - 4\cos\theta \cdot \sqrt{3}\, \frac{\partial \mu_{CH}^{(2)}}{\partial \varphi_1} \cdot \frac{1}{r_{CH}} + 2\sqrt{3}\, \frac{\partial \mu_{CH}}{\partial \varphi_1} \right] E_l^{A_1} \right\};$$

(10a)

$$\frac{\partial P_\xi}{\partial Q_l^{A_1}} = \frac{\partial P_\eta}{\partial Q_l^{A_1}} = 0; \quad (l = 1, 2, 3),$$

$$\frac{\partial P_\eta}{\partial Q_l^{EII}} = \sum \frac{\partial P_\eta}{\partial S_k^E} L_{kl} = \left\{ \left[\sin\theta \sqrt{\frac{3}{2}}\, \frac{\partial \mu_{CH}^{(1)}}{\partial q_1} - \sin\theta \sqrt{\frac{3}{2}}\, \frac{\partial \mu_{CH}^{(2)}}{\partial q_1} - \right.\right.$$

$$- \cos\theta \sqrt{\frac{3}{2}}\, \mu_{CH} \left(\frac{\partial \varphi_1}{\partial q_1} - \frac{\partial \varphi_2}{\partial q_1} \right) \Bigg] C_{ql}^{EII} + \left[-\cos\theta \cdot \sqrt{\frac{3}{2}}\, \frac{\mu_{CH}}{r_{CH}} + \right.$$

$$+ 2\sin\theta \cdot \sqrt{\frac{3}{2}}\, \frac{\partial \mu_{CH}^{(1)}}{\partial \varphi_1} \frac{1}{r_{CH}} - 2\sin\theta \sqrt{\frac{3}{2}}\, \frac{\partial \mu_{CH}^{(2)}}{\partial \varphi_1} \frac{1}{r_{CH}} \Bigg] E_l^{EII} +$$

(10b) $$+ \left. \left[-\sin\theta \cdot \sqrt{\frac{3}{2}}\, \frac{\mu_{CH}}{r_{CH}} \right] F_l^{EII} + \frac{\mu_{CZ}}{r_{CH}} G_l^{EII} \right\};$$

$$\frac{\partial P_\xi}{\partial Q_l^{EII}} = \frac{\partial P_\zeta}{\partial Q_l^{EII}} = 0 \quad (l = 4, 5, 6).$$

4. The form of the vibrations necessary for carrying out the calculation of the intensities was taken by us from reference [7], in which the non-tetrahedral geometry of the CX_3Z molecule and frequencies of normal vibrations were used, corrected for Fermi resonance and anharmonicity. In this work a table of coefficients L_{lk}^{-1}, which connect Q_l and S_k, was presented. However in verifying this table (on the basis of using the theoretical relation $\| L \| \cdot \| L^* \| = \| A_{ij} \|$, where $\| A_{ij} \|$ is the matrix of kinetic coefficients) it was shown that there are some misprints in it, so we made the necessary corrections in the table. On treating the matrices $|L_{lk}^{-1}|^{A_1}$ and $|L_{lk}^{-1}|^{E}$ we obtained the coefficients $C_{ol}^{A_1}$, $C_{qe}^{A_1}$ and $D_{\alpha l}^{A_1}$ (in article [8] in place of α^{A_1} another coefficient was used, S_2, which is a combination of α and δ, but we made the transition from S_2 to α^{A_1}) and C_{ql}^{E}, $D_{\alpha l}^{E}$, $D_{\delta l}^{E}$. Using these coefficients, with the help of formulae (4-9) we calculated the coefficients $E_l^{A_1}$, E_l^{EII}, F_l^{EII}, G_l^{EII} (see table 1).

Table 1

Coefficients C_e, E_e, F_e, G_e (type A and E II) of Methyl Halides (in units $10^{12} g^{-2}$)

Molecule	Coordinates	Symmetry type A_1			Coordinates	Symmetry type E II		
		q_1	q_2	q_3		q_4	q_5	q_6
CH_3Cl	q	0,7769	0,0851	0,0144	q	0,816	0,0163	0,0113
	φ	0,1505	−0,8515	−0,0861	φ	−0,0421	0,3111	0,6806
	φ_0	−0,0457	0,0714	0,2454	ψ	−0,0781	−0,7373	0,3474
	—	—	—	—	∞	0,0446	0,0278	−0,0902
CD_3Cl	q	0,5531	0,0797	0,011	q	0,606	−0,0009	0,0165
	φ	0,1709	−0,6456	0,0216	φ	−0,0457	0,1748	0,4992
	φ_0	−0,0684	0,1192	0,2202	ψ	−0,1254	−0,5576	0,2139
	—	—	—	—	∞	0,0616	0,0381	−0,0684
CH_3Br	q	0,7799	0,0476	0,0078	q	0,8156	0,0099	0,0038
	φ	0,1067	−0,8483	−0,0078	φ	−0,0579	0,3833	0,6582
	φ_0	−0,0695	0,0751	0,225	ψ	−0,0973	−0,6983	0,4212
	—	—	—	—	∞	0,0424	0,021	−0,0494
CD_3Br	q	0,5565	0,0474	0,0076	q	0,6057	−0,0046	0,0121
	φ	0,1211	−0,6478	−0,0069	φ	−0,0582	0,2425	0,4762
	φ_0	−0,0684	0,1162	0,2022	ψ	−0,1379	−0,5223	0,2852
	—	—	—	—	∞	0,0578	0,0277	−0,0666
CH_3I	q	0,776	0,0871	0,0132	q	0,8163	0,014	0,0025
	φ	0,1684	−0,9543	−0,0558	φ	−0,0337	0,367	0,6723
	φ_0	−0,0446	0,0782	0,2164	ψ	−0,0774	−0,7089	0,4073
	—	—	—	—	∞	0,0365	0,0212	−0,0426
CD_3I	q	0,5524	0,0783	0,0106	q	0,6067	0,0006	0,0071
	φ	0,1874	−0,7246	0,0026	φ	−0,0402	0,2389	0,4872
	φ_0	−0,065	0,1139	0,1942	ψ	−0,1216	−0,5303	0,2781
	—	—	—	—	∞	0,0501	0,0276	−0,0491

The following parameters were used for the calculation [7]:

CH_3Cl: r_{CH}=1.097 Å; r_{CCl}=1.78 Å; ∠HCH=111°30′; ∠HCCl = 107°21′.

CH_3Br: r_{CH}=1.09 Å; r_{CBr} =1.936 Å; ∠HCH=111°44′; ∠HCBr = 107°4′.

CH_3I: r_{CH}=1.092 Å; r_{CI} =2.139 Å; ∠HCH = 112°7′; ∠HCI = 106°40′.

Placing in formula (10) the values found experimentally [5] for $\frac{\partial P}{\partial Q_l}$ and coefficients C_l, E_l, F_l, G_l and solving the system of equations obtained, we obtain the derivatives of the dipole moment according to the coordinates of symmetry $\frac{\partial P}{\partial S_k}$ of the molecules CH_3Z and CD_3Z. In table 2

**In the zero approximation

$$\frac{\partial \mu_{CH}}{\partial q_o} = \frac{\partial \varphi_1}{\partial q_o} = \frac{\partial \mu_{CH}^2}{\partial q_1} = \frac{\partial \mu_{CZ}}{\partial q_1} = \frac{\partial \varphi_1}{\partial q_1} = \frac{\partial \varphi_2}{\partial q_1} =$$

$$= \frac{\partial \mu_{CH}^{(1)}}{\partial \varphi_1} = \frac{\partial \mu_{CH}^{(2)}}{\partial \varphi_1} = \frac{\partial \mu_{CZ}}{\partial \varphi_1} = 0$$

and in the case of tetrahedral angles our formulae transpose into the corresponding formulae (22.39) and (22.41) of the monograph [6].

are presented an average of the values $\frac{\partial P}{\partial S^{A_1}}$ for light and heavy (hydrogen) molecules, which correspond to the four different combinations of the signs $\frac{\partial P}{\partial Q_i}$ (as is well known, values for $\left[\frac{\partial P}{\partial Q_i}\right]^2$, are determined experimentally hence for each value $\frac{\partial P}{\partial Q_i}$ there are two possibilities [with sign (+) or (-)]. The designations in table 2 have the following meanings: for example, (+ + -) means that the derivatives $\frac{\partial P}{\partial Q_1}$ and $\frac{\partial P}{\partial Q_2}$ have the (+) sign, while the derivative $\frac{\partial P}{\partial Q_3}$ has the (-) sign. In the other four combinations of signs $\frac{\partial P}{\partial Q_i}$ corresponds to $\frac{\partial P}{\partial S^{A_1}}$, distinguished from those presented in table 2 only by sign. As concerns the values $\frac{\partial P}{\partial S^E}$ for the E type of symmetry, there are three equations for calculating the four values of $\frac{\partial P}{\partial S^E}$.

Table 2

Derivatives of the Dipole Moment in Symmetry Coordinates $\frac{\partial P_\zeta}{\partial S^{A_1}}$ (in units D/Å)(Symmetry type A_1)

Molecule	$\frac{\partial P_\zeta}{\partial S}$	(+ + +)	(+ + -)	(+ - +)	(+ - -)
CH_3Cl and CD_3Cl	$\frac{\partial P}{\partial q}$	1.0001	0.7665	0.7481	0.5145
	$\frac{\partial P}{\partial \gamma}$	−0.0924	−0.7038	0.863	0.2517
	$\frac{\partial P}{\partial q_0}$	2.1723	−2.301	2.229	−2.2443
CH_3Br and CD_3Br	$\frac{\partial P}{\partial q}$	0.8631	0.7089	0.6537	0.4875
	$\frac{\partial P}{\partial \gamma}$	−0.3225	−0.75	0.8325	0.405
	$\frac{\partial P}{\partial q_0}$	1.4633	−1.6746	1.6389	−1.501
CH_3I and CD_3I	$\frac{\partial P}{\partial q}$	0.752	0.634	0.4329	0.3648
	$\frac{\partial P}{\partial \gamma}$	−0.4529	−0.6193	0.7241	0.5577
	$\frac{\partial P}{\partial q_0}$	0.588	−0.8003	0.7476	−0.6408

And so, in order for the problem to be simple, it is necessary to be given a value for the dipole moment of the carbon-halogen bond μ_{CZ}. We shall agree to consider the dipole moment as positive in that case where the dipole is directed from the end atom Z or X (where the negative end of the dipole is placed) towards the central carbon atom (where the positive end of the dipole is placed). In the case of the methyl halides it is possible, on sufficient grounds, to assume that the dipole moment μ_{CZ} has a positive value. The dipole moment of the bond C-Z is determined by the formula

$$\mu_{CZ} = \mu_{CH_3Z} + 3 \cos\theta \cdot \mu_{CH}.$$

The dipole moments of the methyl halides are known: [5]

$$\mu_{CH_3Cl} = 1.87 \text{ D}, \quad \mu_{CH_3Br} = 1.8 \text{ D}, \quad \mu_{CH_3I} = 1.62 \text{ D}.$$

Using μ_{CZ} in (10b) we obtain a system of equations from which dP/dS^E is calculated according to the formula:

$$\frac{\partial P_\eta}{\partial S^E} = \sum_{i=4}^{6} (L^{-1})_{1k} \left[\frac{\partial P_\eta}{\partial Q_i} - G_i \mu_{CZ}\right]$$

Table 3

Derivatives of the Dipole Moment in Symmetry Coordinate $\frac{\partial P_\eta}{\partial S^{E\,II}}$ (in units D/Å)(Symmetry type E II)

Molecule	$\frac{\partial P_\eta}{\partial S}$	(+ + +)	(+ + -)	(- + +)	(+ - +)	(+ - -)	(- + -)	(- - +)	(- - -)
CH_3Cl and CD_3Cl	$\frac{\partial P}{\partial q}$	0.1959	0.1485	−0.4543	0.3107	0.2633	−0.5016	−0.3395	−0.3868
	$\frac{\partial P}{\partial \gamma}$	0.4755	0.1194	0.492	0.112	−0.2448	0.136	0.1278	−0.2282
	$\frac{\partial P}{\partial t}$	−0.1344	−0.2635	−0.1352	0.5203	0.3912	−0.2643	0.5195	0.3904
CH_3Br and CD_3Br	$\frac{\partial P}{\partial q}$	0.1171	0.0337	−0.3107	0.2239	0.1405	−0.3941	−0.204	−0.2873
	$\frac{\partial P}{\partial \gamma}$	0.5202	0.0768	0.54	0.0828	−0.3806	0.0666	0.1025	−0.3409
	$\frac{\partial P}{\partial t}$	−0.0652	−0.3163	−0.0868	0.5272	0.306	−0.308	0.5355	0.3144
CH_3I and CD_3I	$\frac{\partial P}{\partial q}$	0.0532	−0.0203	−0.2206	0.1495	0.0759	−0.2941	−0.1243	−0.1979
	$\frac{\partial P}{\partial \gamma}$	0.5241	−0.0071	0.5275	0.1349	−0.3964	−0.0038	0.1383	−0.393
	$\frac{\partial P}{\partial t}$	−0.0861	−0.3348	−0.0878	0.5125	0.2638	−0.3363	0.5109	0.2622

Since we chose definite values for μ_{CZ}, it then follows that we defined not only the values $\frac{\partial P}{\partial S^E}$, but also their signs, because $\left[\frac{\partial P}{\partial Q_i} - G_i \mu_{CZ}\right]$ have different values for different signs of $\frac{\partial P}{\partial Q_i}$. In table 3 average values of $\frac{\partial P}{\partial S^E}$ are presented for CH_3Z and CD_3Z corresponding to the eight different combinations of signs of $\frac{\partial P_\eta}{\partial Q_i}$ (designations have the same meaning in table 2).

In order to choose the correct values for $\frac{\partial P_\zeta}{\partial S^{A_1}_k}$ (from four possible variants) and for $\frac{\partial P_\eta}{\partial S^E_k}$ (from eight possible variants) we insert $\frac{\partial P}{\partial S^{A_1}_k}$, and $\frac{\partial P}{\partial S^E}$ in (10a) and (10b) and calculate $\frac{\partial P}{\partial Q_i}$ for CH_3Z and CD_3Z (see tables 4-6). It is necessary to choose those values of $\frac{\partial P}{\partial S}$ for which calculated values of $\frac{\partial P}{\partial Q_i}$ best correspond with experimental values of $\frac{\partial P}{\partial Q_i}$ simultaneously for CH_3Z and CD_3Z.

Table 4

Derivatives of the Dipole Moment in the Normal Coordinate $\frac{\partial P_i}{\partial Q_e}$ of CH_3Cl and CD_3Cl (in units $\frac{CGSE}{cm.g^{\frac{1}{2}}}$)

Frequency (cm^{-1})	Symmetry	$\frac{\partial P_i}{\partial Q_e}$	CH_3Cl										
			Experimental	+ + +	+ + −	− + +	+ − −	− + −	− − +	− − −	+ − +	Error (in %)
3209	E	$\frac{\partial P_{\parallel}}{\partial Q_4}$	26.97 ± 0.83	20.86	19.5	-32.26	25.29	-33.61	-26.47	-27.83	26.64	1.2
1520	E	$\frac{\partial P_{\parallel}}{\partial Q_5}$	30.27 ± 0.67	28.65	27.02	28.17	-32.4	26.53	-31.25	-32.88	-30.76	1.6
1049	E	$\frac{\partial P_{\parallel}}{\partial Q_6}$	17.21 ± 0.17	20.52	-8.61	20.9	-10.89	-8.23	18.62	-10.5	18.24	6
3062	A_1	$\frac{\partial P_{\perp}}{\partial Q_1}$	56.25 ± 0.89	66.37	59.47		54.02				60.92	4
1398	A_1	$\frac{\partial P_{\perp}}{\partial Q_2}$	31.62 ± 1.1	31.9	50.03		33.07				-51.2	4.6
733	A_1	$\frac{\partial P_{\perp}}{\partial Q_3}$	57.5 ± 0.57	55.34	-50.71		-55.99				50.06	2.6
							CD_3Cl					
2379	E	$\frac{\partial P_{\parallel}}{\partial Q_4}$	19.46 ± 0.47	19.29	19.77	-20.19	20.29	-19.7	-19.66	-19.28	19.81	1.8
1092	E	$\frac{\partial P_{\parallel}}{\partial Q_5}$	22.55 ± 2.25	20.77	21.75	21.17	-21.13	22.14	-21.72	-20.74	-22.11	1.9
750	E	$\frac{\partial P_{\parallel}}{\partial Q_6}$	8.98 ± 2.5	12.24	-8.37	11.98	-12.36	-8.63	7.99	-12.62	8.26	8
2207	A_1	$\frac{\partial P_{\perp}}{\partial Q_1}$	46.42 ± 1.15	38.88	46.1		48.11				40.89	3.6
1054	A_1	$\frac{\partial P_{\perp}}{\partial Q_2}$	39.63 ± 2.46	39.84	24.12		-38.9				-23.18	1.8
696	A_1	$\frac{\partial P_{\perp}}{\partial Q_3}$	46.8 ± 1.15	48.74	-51.34		-48.31				51.77	3.2

Table 5

Derivatives of the Dipole Moment in the Normal Coordinate $\frac{\partial P_i}{\partial Q_e}$ of CH_3Br and CD_3Br (in units $\frac{CGSE}{cm.g^{\frac{1}{2}}}$)

Frequency (cm^{-1})	Symmetry	$\frac{\partial P_i}{\partial Q_e}$	CH_3Br									
			Experimental	+ + +	+ + −	− + +	+ − −	− + −	− − +	− − −	+ − +	Error (in %)
3213	E	$\frac{\partial P_{\parallel}}{\partial Q_4}$	18.51 ± 0.33	12.78	10.70	-22.31	16.47	-24.39	-17.12	-19.2	17.97	2.9
1506	E	$\frac{\partial P_{\parallel}}{\partial Q_5}$	29.8 ± 0.4	29.32	27.64	29.07	-32.35	27.39	-30.92	-32.60	-30.68	2.9
975	E	$\frac{\partial P_{\parallel}}{\partial Q_6}$	22.88 ± 0.23	24.44	-14.34	24.64	-16.57	-14.14	22.42	-16.36	22.22	2.9
							CD_3Br					
2381	E	$\frac{\partial P_{\parallel}}{\partial Q_4}$	12.64 ± 0.3	12.64	13.21	-13.51	13.64	-12.93	-13.07	-12.50	13.07	3.4
1084	E	$\frac{\partial P_{\parallel}}{\partial Q_5}$	22.75 ± 0.77	21.00	21.84	21.24	-21.32	22.08	-21.92	-21.08	-22.16	2.6
730	E	$\frac{\partial P_{\parallel}}{\partial Q_6}$	12.1 ± 0.3	15.33	-12.36	15.13	-15.10	-12.56	+12.39	-15.30	12.59	4

Table 5 (continued)

Derivatives of the Dipole Moment in the Normal Coordinate $\frac{\partial P_i}{\partial Q_e}$ of CH_3Br and CD_3Br (in units $\frac{CGSE}{cm.g^{\frac{1}{2}}}$)

Frequency (cm-1)	Symmetry	$\frac{\partial P_i}{\partial Q_e}$	CH_3Br					
			Experimental	+ + +	+ + −	+ − +	+ − −	Error (in %)
3061	A_1	$\frac{\partial P_x}{\partial Q_1}$	52.04 ± 2.18	58.09	53.74	53.40	49.05	5.7
1332	A_1	$\frac{\partial P_z}{\partial Q_2}$	45.04 ± 0.77	42.45	54.41	-55.22	-43.26	3.9
614	A_1	$\frac{\partial P_z}{\partial Q_3}$	35.16 ± 1.12	35.78	-32.05	31.70	-36.13	2.8
			CD_3Br					
2196	A_1	$\frac{\partial P_z}{\partial Q_1}$	39.65 ± 1.00	35.25	39.30	37.72	41.77	5.3
1002	A_1	$\frac{\partial P_z}{\partial Q_2}$	40.30 ± 0.93	41.99	32.48	-31.81	41.32	2.5
580	A_1	$\frac{\partial P_z}{\partial Q_3}$	31.06 ± 0.77	30.27	-33.26	33.52	30.01	3.4

Table 6

Derivatives of the Dipole Moment in the Normal Coordinate $\frac{\partial P_i}{\partial Q_e}$ of CH_3J and CD_3J (in units $\frac{CGSE}{cm.g^{\frac{1}{2}}}$)

Frequency (cm-1)	Symmetry	$\frac{\partial P_i}{\partial Q_e}$	CH_3J									
			Experimental	+ + +	+ + −	− + +	+ − −	− + −	− − +	− − −	+ − +	Error (in %)
3229	E	$\frac{\partial P_y}{\partial Q_4}$	12.72 ± 0.38	7.30	5.01	-15.05	9.54	-17.34	-10.51	-12.81	11.83	7
1504	E	$\frac{\partial P_y}{\partial Q_5}$	28.08 ± 0.42	27.74	25.72	27.59	-30.74	25.57	-28.88	-30.89	-28.73	2
906	E	$\frac{\partial P_y}{\partial Q_6}$	25.56 ± 0.36	27.02	-18.84	27.12	-20.60	-18.74	25.35	-20.51	25.26	1
3060	A_1	$\frac{\partial P_x}{\partial Q_1}$	43.07 ± 2.6	48.11	46.22		40.55				42.45	5.8
1288	A_1	$\frac{\partial P_z}{\partial Q_2}$	55.05 ± 1.32	54.37	58.79		-55.06				-59.48	0
533	A_1	$\frac{\partial P_z}{\partial Q_3}$	16.59 ± 0.17	16.24	-12.96		-16.50				12.71	0.5
			CD_3J									
2400	E	$\frac{\partial P_y}{\partial Q_4}$	7.16 ± 0.35	7.72	8.42	-8.88	8.54	-8.19	-8.76	-8.07	7.85	9.6
1083	E	$\frac{\partial P_y}{\partial Q_5}$	21.44 ± 2.14	19.73	20.65	19.88	-20.08	20.79	-20.85	-19,93	-20.99	2.1
676	E	$\frac{\partial P_y}{\partial Q_6}$	15.26 ± 0.76	17.74	-15.11	17.66	-17.36	-15.19	15.41	-17.44	15.49	1.5
2210	A1	$\frac{\partial P_z}{\partial Q_1}$	32.95 ± 0.76	29.23	31.38		34.77				32.62	5.5
975	A_1	$\frac{\partial P_z}{\partial Q_2}$	44.87 ± 1.88	45.41	41.11		-44.86				-40.56	0
502	A_1	$\frac{\partial P_z}{\partial Q_3}$	11.84 ± 0.24	12.09	-44.98		-11.91				15.17	0.6

Table 7

Electro-optical Parameters of the Methyl Halides (in units D/Å)

	CH_3Cl, CD_3Cl		CH_3Br, CD_3Br		CH_3J, CD_3J	
	E (+ - +)		E (+ - +)		E (+ - +)	
μ_{CH} (in units D)	-0.4882		-0.4908		-0.477	
μ_{CH}/r_{CH}	-0.4451		-0.4503		-0.4368	
μ_{CZ} (in units D)	1.4333		1.3679		1.2096	
μ_{CZ}/r_{CZ}	0.8052		0.7066		0.5655	
$\left[\left(\frac{\partial\mu_{CH}^{(1)}}{\partial q_1}-\frac{\partial\mu_{CH}^{(2)}}{\partial q_1}\right)-\cot\theta\cdot\mu_{CH}\left(\frac{\partial\varphi_1}{\partial q_1}-\frac{\partial\varphi_2}{\partial q_1}\right)\right]$	0.2657		0.1912		0.1274	
$\frac{1}{r_{CH}}\left(\frac{\partial\mu_{CH}^{(1)}}{\partial\varphi_1}-\frac{\partial\mu_{CH}^{(2)}}{\partial\varphi_1}\right)$	-0.022		-0.0338		-0.0079	
	$A_1(- - -)$	$A_1(- - -)$	$A_1(- - -)$	$A_1(- - -)$	$A_1(- - -)$	$A_1(- - -)$
$\frac{1}{r_{CH}}\left(\frac{\partial\mu_{CZ}}{\partial\varphi_1}-3\cos\theta\cdot\frac{\partial\mu_{CH}^{(2)}}{\partial\varphi_1}\right)$	-0.1463	-0.2916	-0.1082	-0.3421	-0.0505	-0.3725
$\left[\frac{\partial\mu_{CZ}}{\partial q_1}-3\cos\theta\frac{\partial\mu_{CH}^{(2)}}{\partial q_1}-\operatorname{csc}\theta\cdot\mu_{CH}\frac{\partial\varphi_1}{\partial q_1}+(\operatorname{csc}\theta-3\sin\theta)\mu_{CH}\frac{\partial\varphi_2}{\partial q_1}\right]$	0.3763	-0.2178	0.3434	-0.2411	0.2472	-0.1741
$\left[\frac{\partial\mu_{CZ}}{\partial q_o}-3\cos\theta\frac{\partial\mu_{CH}}{\partial q_o}-3\sin\theta\cdot\mu_{CH}\frac{\partial\varphi_1}{\partial q_o}\right]$	-2.2443	2.2443	-1.501	1.501	-0.6408	0.6408

As follows from tables 4 - 6, the best agreement is obtained for the following combination of signs of $\frac{\partial P}{\partial q_i}$: for the type of symmetry A_1-(+--) or (-++), for the symmetry type E -(+-+). Using values of $\frac{\partial P}{\partial S}$ corresponding to these variants we obtained a system of electro-optical parameters of methyl-halides (see table 7). It is necessary to note, with respect to this, that for part of the parameters absolute signs are defined, for three parameters two systems of values were obtained, which correspond to the two possibilities of choice of sign for $\frac{\partial P_z}{\partial q_1^{A1}}$. We much prefer to use the system which corresponds to the combination of signs of $\frac{\partial P_z}{\partial q_i^{A1}}$ (+ - -) for the following reasons. The parameter $\frac{1}{r_{CH}}\left(\frac{\partial\mu_{CH}^{(1)}}{\partial\varphi_1}-\frac{\partial\mu_{CH}^{(2)}}{\partial\varphi_1}\right)$ has a small value, therefore we can expect that the parameter of the same type $\frac{1}{r_{CH}}\left(\frac{\partial\mu_{CZ}}{\partial\varphi_1}-3\cos\theta\cdot\frac{\partial\mu_{CH}^{(2)}}{\partial\varphi_1}\right)$ also ought to have a comparatively small value. Only the first variant satisfies this requirement. In addition, under conditions of the indicated choice this parameter will naturally diminish on going from chloroform to iodoform (as do the majority of the other parameters), while in the second variant it would increase.

It follows from examination of table 7 that with a reduction of the electronegativity of the halogen the majority of parameters naturally diminish. Two parameters fall out of this regularity somewhat $\frac{\mu_{CH}}{r_{CH}}$ and $\frac{1}{r_{CH}}\left(\frac{\partial\mu_{CH}^{(1)}}{\partial\varphi_1}-\frac{\partial\mu_{CH}^{(2)}}{\partial\varphi_1}\right)$ (which change very insignificantly in absolute value), which originally increase, but subsequently decrease again. This deviation might be attributed to the inexactness of the experiment.

In all the metal halides the negative end of the dipole μ_{CH} is found on the carbon atom, while the positive end is found on the hydrogen atom.

Further, from table 7 it is evident that derivatives $\frac{\partial\mu_{CH}^{(1)}}{\partial q_1}$ (under condition of the smallness of $\frac{\partial\mu_{CH}^{(2)}}{\partial q_1}$, $\frac{\partial\varphi}{\partial q}$) and $\frac{\partial\mu_{CZ}}{\partial q_o}$ (under condition of smallness of $\frac{\partial\mu_{CH}}{\partial q_o}$, $\frac{\partial\varphi}{\partial q_o}$) have negative values. This means that under the condition of increasing the length of the CH and CZ bonds relative to the equilibrium spacing their dipole moments decrease.

July 5, 1958

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Investigation of the Temperature Dependence of the Infrared Absorption Band Intensity in Liquids

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Abstract: Quantitative measurements were made of the intensity of infrared absorption bands of a series of liquids at different temperatures. It was discovered that there is a divergence from the dependence deduced theoretically. The effect which was found is discussed.

According to theory [1] based on purely statistical ideas, the intensity of vibrational spectral lines ought to increase with an increase in temperature. However, experimental data from a series of papers, carried out principally for Raman spectra of materials in the liquid phase [2-9] show that, as a rule, the thermal change of intensity is in the opposite direction.

There are very few investigations of temperature dependence of infrared absorption bands;* here we can only refer to a few relevant works [10-14]. This is probably connected with the relatively more difficult technique of infrared measurements. In this work further study of the temperature dependence of the intensities of vibrational spectra of molecules was undertaken, to wit, the infrared absorption of liquids. In the quantitative treatment of the experimental results a great deal of attention was paid to the method of measurement of the intensity.

EXPERIMENTAL METHOD

The experimental part of the work was carried out on a double-beam IKS-2 spectrometer. In order to avoid distortion of the recording equipment, the linearity of the photometric wedge was tested. Recording of the spectrum was carried out at sufficiently slow rates [15].

The apparatus for temperature investigations (fig. 1, a) consisted of a glass vessel 1 with rock salt windows 2. Inside the vessel was a metal container 4 with cells for the material to be examined. The horizontal ground end 3 between container and vessel was cooled by running water. During the work a vacuum of 10^{-3} mm. Hg was created. Cooling of the cell was achieved by liquid or gaseous nitrogen; heating was done with hot air. The temperature was measured with a thermocouple 5 and regulated by a mercury thermoregulator with an average precision of ± 2-3° C. Variation of temperature between upper and lower parts of the cell did not exceed 2° C.

For investigations of liquids, cells of constant thickness were used (fig. 1, b). The cells consisted of two rock salt plates 6 fastened ** in a demountable holder 7. The center of one plate, surrounded by a circular groove, was polished to the necessary depth. In order to achieve the hermetic seal necessary for the temperature measurements, the lateral edges 8 were treated with a melt of polyamide resin (kapron, softening temperature = $+230^{\circ}$ C.). The salt did not crack during this treatment if cooling was slow enough (two hours). It is necessary to note that the resin used in the work was distinguished by its exceptional chemical inertness and substantial mechanical strength. Introduction of samples was done through two openings 9 (diameter = 1 mm.) which were closed by two plugs 10. As plugs silicoorganic resins (silicone) were used; they are well known for their thermal and chemical stability.

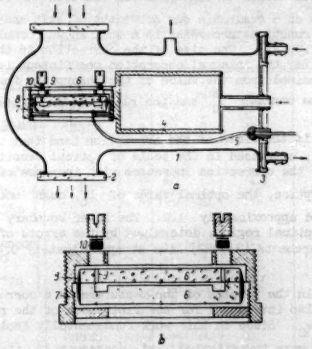

Figure 1. a - apparatus for temperature investigations; b - cell for temperature investigations.

The cells described were used in a wide range of temperatures, approximately from -100 to $+180^{\circ}$ C.

Cells for temperature measurements are described in the literature [16]. However the apparatus we used is simple to make and more convenient for our purposes in the temperature interval investigated.

The thickness of the cell was determined by an interference method [17]. For cells which did not give a clear-cut interference pattern a method of graduating according to optical density was used. In this case cells of known thickness measured by interference were used as standards, while the broadest absorption bands for carrying out the graduation were chosen to minimize departure from

* We are not putting here works devoted sufficiently to the study of temperature effects of rotational isomers and hydrogen bonding.

** In this respect the holder should not strongly compress the cell, since owing to its elastic properties, and also the different coefficients of linear expansion of metal and salt, a change in the effective working thickness of the cell with temperature might take place (of the order of several microns at 100° C.).

Lambert's law. The precision reached in the determination of the effective working films of the liquids investigated lay within the limits of 5-15%, depending on the measured thickness.

In the quantitative measurement of the temperature dependence of intensity of absorption bands, the question of method has great importance since true change of intensity in the general case might be distorted by apparatus or other influences. The apparatus distortion depends, basically, on the finiteness of the width of the slit. The influence of the corresponding apparatus functions on the intensity and form of the spectral lines has not once been considered in the literature [18, 19]. In our work the values of the corrections on the slit were calculated with the help of the Voigt function, assuming that the apparatus function has a Gaussian form, while the true contour of the absorption band is expressed by a dispersion distribution. Special investigations were carried out which confirmed the correctness of the assumption concerning the dispersion distribution of the true contour. A more detailed discussion of this question is given in reference [20].

The width of the apparatus function $\delta\nu$ was found as a quadratic sum of widths of slit and non-slit functions according to a well known formula [18, 19, 21]. The size of the correction to the slit for the integral absorption coefficient is determined from the value of the absorption found at the maximum D_0^H and the ratio $\delta\nu/\Delta\nu_D^H$, where $\Delta\nu_D^H$ is the width of the absorption band that was found, expressed in the scale of optical density. Since the correction increases with increase of absorption, the optimal value of D_0^H ought not to exceed approximately 1.2. The lower boundary of the optimal region, determined by the errors of the measurements [21, 22] lies at approximately 0.4 for D_0^H.

In the results of the measurements a correction was also introduced for the finiteness of the region $\nu_1 - \nu_2$. Since in this work fundamentally isolated bands were investigated, and, consequently, it is possible to draw precisely lines of the background (lines of 100% transmission), then, in practice, the correction was introduced only for the wings of integrated bands. The correction to the wings for the bands found, which take a form intermediate between the Gaussian and dispersion distributions, was specially intended for different forms and different regions of integration [20]. It is convenient to characterize the form of the contour in this circumstance by the form index r_H, which is defined as

$$r_H = \frac{D_\infty^H}{\Delta\nu_D^H \cdot D_0^H}, \qquad (1)$$

where D_∞^H is the integral band intensity. Then for the infrared absorption bands found, the index r_H evidently lies within the limits

$$1.065 \leqslant r_H \leqslant 1.57.$$

Since the experimental determination of the form index (by the method of successive approximations) is attended by great lack of precision, therefore r_H is only calculated for the given conditions of measurement under the assumption of dispersion of the true contour [20].

In the temperature measurements the change in density of the liquid was further taken into account. The expansion of the cells themselves with temperature changes their working thickness less than 1% at 100° C., and therefore was disregarded in this work.

However, as was detected, it is necessary to take into account the change of thickness of the cell due to its elastic properties, which was due to the temperature change of the pressure of the vapors of the liquid being studied. According to experiment such a change of thickness is about 1-2μ at one atmosphere, and may be very important for the thin working film. Since the coefficient of elasticity is little changed in the temperature interval investigated, the size of the correction for elasticity can be described in the following way:

$$\epsilon = \left(1 - \frac{D_{vac.}}{D_{atm.}}\right) \cdot \frac{\Delta p}{760}, \qquad (2)$$

where $D_{vac.}$ and $D_{atm.}$ are optical densities of the bands of the liquid for, respectively, the evacuated cell and the cell at atmospheric pressure; Δp is the change in vapor pressure of the liquid for the temperature interval being investigated.

With the change in temperature of the liquid being studied, its capacity for radiation and reflection are also changed at the sites of the absorption bands. Estimation of the ratio of the intensity of the thermal radiation of the material to the radiation of the source (according to Planck's formula) showed that it is insignificant for all temperatures used. The influence of the reflectance of the material, connected with temperature change of the refractive index, is negligible, as can be shown. Possible small changes of background during the running of the spectra (as a result of a little fogging of the windows of the cells, etc.) were always taken into account as a corresponding displacement of the 100% transmission lines. The usual accidental error in the experimental integral coefficient of absorption, found as the sum of errors in the values of the thickness of the cell and of the recorded area of the band,* was generally 10-20%. The relative change of intensity with temperature was determined with a precision of 5-10%.

RESULTS AND DISCUSSION

A series of liquids, with and without dipoles, which have more or less isolated and not too intense absorption bands in the 3-15 μ region, were taken

*A source of errors in registering the areas of the bands is some operational instability of the receiver-amplifier and motor of the apparatus (~ 2-3%), and also inexact fixing of the temperature of the liquid (~ 0-2%) and error of the planimeter (~ 0.5-1%).

as the objects of the investigation.

Choice of optimal conditions and treatment of the results of measurements corresponded to the method described above. In practice four corrections were introduced for the systematic errors: for the width of the slit ($\epsilon_1 \approx 1 - 10\%$), for the wings of the band ($\epsilon_2 \approx 5 - 10\%$), for the density of the liquid ($\epsilon_3 \approx 5 - 15\%$) and for the elasticity of the cell ($\epsilon_4 \approx 0 - 15\%$). Under these circumstances ϵ_2 and ϵ_3 on the one hand, and ϵ_1 and ϵ_4 on the other usually have opposite signs. The influence of corrections ϵ_1 and ϵ_2 on the relative change of intensity is connected with the broadening of the bands due to temperature. The least influence on the relative change of intensity is shown by the correction for the wings, since the ratio of the region of integration $\nu_1 - \nu_2$ to the width of the band $\Delta\nu_D^H$ was always taken as constant while only the form of the band in its dependence on $\frac{\delta\nu}{\Delta\nu_D^H}$ was changed by temperature. On the other hand, the change in density shows the greatest influence. 3-4 photographs at each temperature have already allowed us to estimate the reproducibility of the recording. For control of the results the measurements were made both while raising and lowering the temperature within the temperature interval used. For illustration of the temperature changes, in figures 2-4 are cited the spectrograms found for the 755 cm^{-1} band of cyclohexanone, the 1093 cm^{-1} band of acetone, and the 3050 cm^{-1} band of chloroform. The curves were converted to the optical density $D(\nu)$.

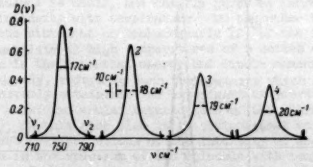

Figure 2. Temperature change of intensity found for the 755 cm^{-1} band of cyclohexanone. 1 - at $-35°$ C.; 2 - at $+25°$ C.; 3 - at $+80°$ C.; 4 - at $+135°$ C.

In tables 1 and 2 are presented the results of measurement of some fundamental vibrations of the investigated dipolar and non-dipolar materials. The integral coefficient of absorption is expressed in a single scale having the dimensions $\left[\frac{cm^2}{mole \cdot sec}\right]$.

For this purpose the correlation was used, where K'_∞ is the measured integral absorption coefficient (in cm^{-2}), c is the velocity of light, M is the molecular weight, and ρ_T is the density of the liquid at the given temperature

$$(3) \qquad K_\infty = K'_\infty \cdot \frac{c \cdot M}{\rho_T} ,$$

In the tables values for K_∞ for each band are given at two extreme temperatures, although in reality measurements were frequently made at 3-4 points of the temperature interval used. If the measurements were taken under conditions of small thicknesses, (~ 4-5μ) determined with significant error, then the corresponding values of K_∞ are not cited.

Table 1

Temperature dependence of intensity of infrared absorption bands of a series of dipolar liquids.

Material	Form and Symmetry of Vibrations	$t°C$	ν_0 cm^{-1}	$\Delta\nu_D$ cm^{-1}	$K_\infty \cdot 10^{-5}$ $\frac{cm^2}{mol \cdot sec}$	$\frac{(K_\infty)_{t_1}}{(K_\infty)_{t_2}}$ (at 100°C)	
						Found	Theor
Acetonitrile CH_3CN p = 3.94D	ν(CC), A_1	− 30	918	6.5	3.8	1.07	0.980
		+ 70	919	10.0	3.55		
	$\delta(CH_3)$, E	− 30	1042	—	18.7	1.18	0.985
		+ 70	1044	—	15.9		
	ν(CN), A_1	− 30	2311	5.5	34.0	1.65	1.000
		+ 70	2312	7.5	20.6		
Nitromethane CH_3NO_2 p = 3.55D	—	− 20	918	5.5	4.35	0.98	0.975
		+ 80	917	9.5	4.45		
	—	− 20	1405	23.0	69.5	1.22	0.980
		+ 80	1403	33.0	57.0		
Cyclohexanone $C_5H_{10}CO$ p = 2.77D	—	− 35	755	11.0	25.9	1.28	0.960
		+135	752	15.0	17.5		
	—	− 35	874	8.5	17.5	1.56	0.970
		+135	873	12.5	9.0		
	—	− 35	920	—	28.2	1.25	0.970
		+135	920	—	19.7		
Acetone $(CH_3)_2CO$ p = 2.73D	δ(HCC)	− 80	908	19.5	17.5	1.09	0.990
		+ 25	911	29.0	16.0		
	$\delta(CH_3)$	− 80	1085	10.0	24.5	1.47	0.995
		+ 25	1093	13.5	16.6		
	ν(CC), B_2	− 80	1240	7.5	—	1.28	1.000
		+ 25	1238	15.0	—		
	ν(CO)	− 80	1713	26.0	—	1.14	1.000
		+ 25	1731	27.5	—		
Methyl Iodide CH_3I p = 1.65D	δ(HCJ), E	− 55	883	22.0	60.0	1.25	0.985
		+ 25	893	34.0	50.0		
	δ(HCH), A_1	− 55	1250	6.0	37.0	1.33	0.995
		+ 25	1261	9.5	29.3		
	ν(HC), A_1	− 55	2966	8.5	18.2	1.22	1.000
		+ 25	2970	11.0	15.5		
Chloroform $CHCl_3$ p = 1.15D	ν(CCl), E	− 50	760	—	—	1.17	0.970
		+ 25	760	—	—		
	δ(HCCl), E	− 50	1231	10.0	—	1.00	0.995
		+ 25	1232	11.0	—		
	ν(CH), A_1	− 50	3047	8.5	30.7	1.97	1.000
		+ 50	3052	9.5	15.6		

Table 2

Temperature dependence of intensity of infrared absorption bands of a series of non-dipolar liquids.

Material	Form and Symmetry of Vibrations	t°C	ν_0 cm^{-1}	$\Delta\nu_D$ cm^{-1}	$K_\infty \cdot 10^{-15}$ cm^2/mole·sec	$\frac{(K_\infty)_{t_1}}{(K_\infty)_{t_2}}$ (at 100° C.) Found	Theor
Cyclo-pentane C_5H_{10}	ν(CC), A	− 75	897	17.0	17.3	1.15	0.985
		+ 25	896	22.0	15.0		
	δ(HCH), E	− 75	1473	17.5	46.0	1.45	1.000
		+ 25	1474	22.5	31.7		
Cyclo-hexane C_6H_{12}	ν(CC), E_u	+ 10	864	12.0	13.5	1.13	0.970
		+ 70	865	16.5	12.5		
	δ(HCH), A_{2u}	+ 10	911	6.0	9.3	0.98	0.985
		+ 70	911	8.0	8.4		
	δ(HCC), E_u	+ 10	1232	7.0	11.9	0.98	0.995
		+ 70	1235	13.0	12.1		
	δ(HCH), E_u	+ 10	1463	11.5	76.5	1.31	1.000
		+ 70	1463	13.0	64.5		
n-Pentane C_5H_{12}	δ(HCC), B''	− 75	727	16.0	8.8	0.91	0.970
		+ 25	728	21.0	9.5		
	δ(HCH), E	− 75	1469	21.0	49.2	0.99	1.000
		+ 25	1469	25.0	49.7		
n-Hexane C_6H_{14}	δ(HCH), E	− 75	1474	17.5	92.5	1.13	1.000
		+ 25	1476	22.0	82.0		
Benzene C_6H_6	δ(HCC), E_{1u}	+ 10	1035	8.5	23.5	1.30	0.985
		+ 70	1036	13.5	20.0		
	ν(CC), E_{1u}	+ 10	1482	5.0	51.7	1.12	0.995
		+ 70	1483	7.0	48.2		
	ν(CH), E_u	+ 10	3034	8.0	69.0	0.87	1.000
		+ 70	3039	11.5	75.0		
p-Xylene $(CH_3)_2C_6H_4$		+ 25	787	8.0	129	1.02	0.980
		+125	788	13.0	127		
Heptene-1 C_7H_{14}	ν(CC)	− 5	1651	7.0	24.8	1.00	0.985
		+ 85	1650	9.0	24.8		

For characterizing the relative change of K_∞ the intensity of each band was taken as unity at the highest temperature investigated. For convenience of comparison the changes of intensity found were reduced everywhere to an interval of 100° C. by using linear interpolation. The theoretical temperature dependence for the fundamental frequencies is defined by a formula of Placzek:

(4)
$$\frac{(K_\infty)_{T_1}}{(K_\infty)_{T_2}} = \frac{1-\exp[-\frac{h\nu}{kT_2}]}{1-\exp[-\frac{h\nu}{kT_1}]}.$$

The temperature dependence of the band displacement (with a precision of ± 1 cm^{-1}) and their broadening (with a precision of ± 1 cm^{-1}) are also shown in the tables. The values of the band width $\Delta\nu_D$ corrected to the width of the slit according to reference [20] are presented in the tables. In those cases where the bands have a forbidden structure, the values of the width are not presented.

As can be seen, for the majority of the bands studied a noticeable discrepancy was found between theoretical and experimental results. Almost all bands show a decrease in intensity with an increase of temperature, while theory predicts an increase in intensity. Frequently departure from theory is rather significant: for example, for the 3050 cm^{-1} band of chloroform, the 2210 cm^{-1} band of acetonitrile, the 1100 cm^{-1} band of acetone, and the 1470 cm^{-1} band of cyclopentane. The frequency dependence of temperature changes of intensity, expressed by formula (4), is also not confirmed. Experiment does not give any kind of definite connection between the changes of intensity found and the magnitude of the absorption quantum. It is evident that the temperature behaviour of the intensity of vibrational spectra of molecules, predicted by statistical theory, in greater or lesser degree, is always exceeded by other temperature dependent influences.

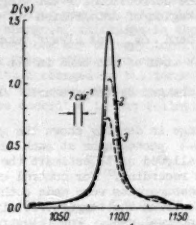

Figure 3. Temperature change of intensity found for the 1093 cm^{-1} band of acetones.
1 - −80° C.; 2 - −30° C.; 3 - +25° C.

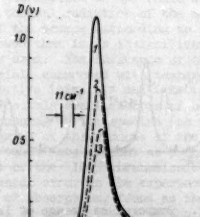

Figure 4. Temperature change of intensity found for the 3050 cm^{-1} band of chlorform.
1 - −50° C.; 2 - 0° C.; 3 - +50° C.

The experimental results of this work, thus, indicate that the discrepancy with theory discovered for Raman spectra also takes place for infrared absorption spectra of liquids. Unfortunately, it is not always possible to compare the results of both methods, since the Raman lines investigated

[3-9] either are forbidden by the rules of selection in infrared absorption, or are awkward to measure. Those very lines which permit the making of a comparison do not, however, give quantitative results. Further, it can be observed that the greater sensitivity towards temperature of the deformational vibrations, compared with stretching noticed in Raman spectroscopy [5,9] does not always take place for infrared absorption spectra. For example, the CH stretching vibrations of chloroform and $C \equiv N$ vibrations of acetonitrile are changed much more strongly with temperature than, for example, the $\delta(CH)$ and $\delta(CH_3)$ vibrations in the same molecules. Similarly multiple bonds are subjected to the influence of temperature no less than simple bonds (example: the strong change of intensity of the $C \equiv N$ triple bond of acetonitrile).

Although the discrepancy between theory and experiment in the temperature dependence of intensity for Raman spectra was already well known earlier, nevertheless up to the present time a definitive interpretation of the observed effect did not exist. First of all, it is clear the effect is not merely apparent; it is not caused by any kind of systematic errors. Calculation and estimation of all possible distorting factors, which were made in the work, definitely point to the fact that the discrepancy has another physical nature, and, in particular, cannot be explained by temperature broadening of the absorption bands [2].

A group of authors [2,5,7,12] suppose that the fundamental cause which explains the temperature dependence that is found must be sought in the internal dynamics of the molecule (anharmonicity, intramolecular interactions etc.) Calculation of the anharmonicity of vibrations in the general case of a polyatomic molecule is very complicated. An estimation carried out by us of the role of the mechanical electrooptical anharmonicity in the case of a diatomic molecule shows, however, that its influence is small, and chiefly gives an increase of intensity with temperature. On the other hand is the statement of Venkatesvarlu [2] of the inapplicability at high temperatures of a series expansion in the potential energy and dipole moment, evidently, refers to such temperatures which are not apparently attainable for experiment in practice. As to intramolecular interactions of the vibrations [12], in this case also it is obvious that we can expect redistributions of the intensity of absorption in the spectrum of the molecule with temperature. Experimental verification of this supposition ought to include simultaneous study of all the vibrations of the molecule, which, in practice, is difficult to carry out in the infrared region. The experimental data obtained, however, show that the single effect of redistribution, if it even takes place, does not offer the possibility of explaining the temperature changes of intensity which were found. Conclusions concerning the role of electronic excited states do not have validity for infrared absorption spectra.

Probably we must consider intermolecular interactions as the most likely explanation for the discrepancies found. Measurements in the vapor phase, for which formulae of statistical theory have been obtained, might serve as first-hand proof of the intermolecular nature of the anomalies in liquids. So far as is known, the corresponding investigations of temperature dependence in gases are utterly lacking. In connection with this, our preliminary results which do not confirm a decrease of intensity with temperature for gases, are of great interest. Thus, for example, bands of chloroform were studied, including the C-H stretching vibration band, which is strongly changed in the liquid, and these do not show a decrease of intensity in the gas when the temperature is raised from room temperature to +275° C. There is little change, in practice, on heating to 250° C., in the integral intensity of a series of bands of acetone, while the 1260 and 2970 cm^{-1} bands of methyl iodide are even noticeably increased in intensity. The results on the temperature measurements in gases will be published soon.

At the present time the mechanism of the influence of intermolecular interactions on the temperature pattern [25,26] that was found is not completely clear. In every case the experimentally obtained data shows that temperature dependence of the intensity of liquids in infrared spectra is connected in a complicated manner with the properties of the internal structure and the external environment of the molecules. For a definitive elucidation of the nature of the influence, and discovery of the corresponding laws, further experimental investigations are necessary.

July 7, 1958

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Spectroscopic Investigation of the Hydrogen Bond in Mercaptans

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Abstract: The infrared absorption spectra of liquid ethyl mercaptan and n-propyl mercaptan and their solutions in CCl_4 were investigated in the 2300-2700 cm^{-1} region. On the basis of changes in the frequency and intensity of the band of the stretching vibration of the SH group a conclusion was reached concerning the existence in aliphatic mercaptans of a bond of the type S-H. . . S. Comparison of the spectra of solutions of propyl mercaptan in chloroform and dipropylsulfide permits the detection of spectroscopic evidence of the perturbation of the SH group through hydrogen and through sulfur. Spectra of propyl mercaptan were also obtained in acetone, dioxane and triethylamine.

The present work is devoted to an investigation by infrared absorption spectra of hydrogen bonds in aliphatic mercaptans (thio alcohols), and also of hydrogen bonds which are formed by the sulfhydryl groups of the mercaptans with solvent molecules.

There is not a single opinion in the literature on the question of the ability of mercaptans to form hydrogen bonds. The idea of the existence of hydrogen bonds in pure mercaptans does not in itself run counter to their chemical properties. The ability of mercaptans and thioethers to join with a halogen and be a member of numerous coordination compounds shows that sulfur can appear to function as an electron donor [1]. The ability of mercaptans to react with alkalis, with the formation of the metal mercaptides, and also the results of an investigation of hydrogen exchange in mercaptans and hydrogen sulfide [2,3] are evidence of the considerable mobility of the hydrogen of the sulfhydryl group. At the same time, recently there has been promulgated an opinion concerning the absence of such in the association of mercaptans [4]. Mercaptans in the absence of ordinary alcohols do not have elevated boiling point temperatures. On the basis of cryoscopic measurements of the molecular weights of aliphatic mercaptans and thiophenols in benzene Lassettre [5] came to the conclusion that hydrogen bonds of the type SH. . S were absent. Analogous conclusions were reached in references [6 and 7]. A method was proposed by Batsanov and Pakhomov [8] according to which they judge concerning the presence of hydrogen bonding by the deviation from additivity in a homologous series of such properties as molar volume or refraction, while mercaptans belong to that class of compounds for which such additivity is observed. The results of physical-chemical investigations of solutions of mercaptans in basic solvents, show a series indicating the formation of hydrogen bonds of the type SH. . . O and SH. . . N [9-12]. This is in agreement with the results of previous spectroscopic investigations. Gordy and Stanford [13] studied the infrared spectra of solutions of some mercaptansin nitrogen-containing solvents. They determined that in spectra of solutions of C_6H_5SH in pyridine and α-picoline the stretching vibration band of the sulfhydryl group was shifted 114 cm^{-1} to lower frequency, which, along with its strongly increasing intensity, points to the formation of the bond SH. . . N. An analogous, although smaller effect was found for solutions of $n\text{-}C_4H_9SH$.

In benzene solutions, however, the shift of the SH band was not observed, whence the authors concluded that association was absent in mercaptans themselves. Cleveland et al. [14] detected in Raman spectra of solutions of C_6H_5SH in dioxane a splitting of the SH band into two bands at 2536 and 2569 cm^{-1}, explained by the formation of the SH. . .O bond. A very similar picture was observed by Wagner et al. [15] in the IR spectrum of a solution of C_6H_5SH in diethylsulfoxide. These data were confirmed in the work of Josien and coworkers [16] devoted to an investigation of the IR spectra of solutions of thiophenol. By the splitting of the SH stretching vibration band the authors demonstrated as a fact the formation of complexes of thiophenol with pyridine, acetone, ethers and aromatic hydrocarbons. The splitting was also found upon dissolving thiophenol and its halogen derivatives [17] in CCl_4, by which experiment the ability of aromatic thio alcohols to associate was demonstrated for the first time. Finally, the existence of the SH. . .S hydrogen bond in molecules derived from dithiophosphoric acid was shown in reference [18], and also with less certainty, in reference [19]. The question concerning the association of aliphatic mercaptans themselves continued to remain vague, since the existence reported earlier of the hydrogen bond which is of interest to us was of the type which can be evoked by increased mobility of the sulfhydryl hydrogen in the thio compounds which were studied.

EXPERIMENTAL PART

The infrared spectra of mercaptans and their solutions were taken on a Perkin-Elmer 12B spectrometer with LiF prisms, an FEOU-18 amplifier and EPP-09 potentiometer as registering system. The spectral slit width was 2.8 cm^{-1} at 2500 cm^{-1}. Cuvettes of constant thickness, measured on an interferometer, and demountable cuvettes with rings and inserts were used. The integral absorption coefficient $K = \frac{1}{cd}\int \ln \frac{I_0}{I}\, d\nu$ of the stretching vibration band of the SH group was determined planimetrically. The indicated band was located between the band of atmospheric CO_2 at about 2360 cm^{-1} and the usual position of mercaptans in the region of 2650-2700 cm^{-1}. This hampers reduction to zero, and magnifies the error in determining the optical density, which, in even the most unfavorable cases, does not exceed 10-15%. The standard compounds n-propyl mercaptan and n-dipropylsulfide were fractionated on a column. The fractions used in this work were for $n\text{-}C_3H_7SH$, $T^{\circ}_{b.p.} = 67.9^{\circ}$ C., for $(n\text{-}C_3H_7)_2S$, $n_D^{20} = 1.4384$, and $T^{\circ}_{b.p.} = 141.5\text{-}141.6^{\circ}$ C., $n_D^{20} = 1.4513$. Other compounds used were purified by the usual chemical methods.

and fractionations. Solutions were made up by weight. Spectra were taken at room temperature.

Table 1

Frequencies and intensities of the bands of valence vibration of the SH group in spectra of solutions of C_2H_5SH and $n\text{-}C_3H_7SH$ in CCl_4.

Concentration (Moles./l)	ν(SH) (in cm^{-1})	K (in l/mole·cm^{-2})
	Ethyl Mercaptan	
13.5	2561	690
8.27	2565	620
4.35	2573 *	300
2.15	2582 *	230
1.24	2584 *	150
0.185	2584	100
0.171	2584	90
0.096	2584	85
	Propyl Mercaptan	
11.2	2564	790
7.70	2565	490
3.68	2575 *	370
2.69	2563 2582	300
1.54	2583 *	160
0.134	2583	140
0.0537	2583	120

* High frequency component of double bands.

RESULT

Infrared absorption spectra of liquid ethyl mercaptan and normal propyl mercaptan and their solutions in carbon tetrachloride were studied in the region 2400-2700 cm^{-1}. In the surveys of solutions the thickness of the cuvette was selected in such a way that the optical density at the absorption maximum was not less than 1.0-1.5. In table 1 are presented data on the frequencies ν(SH) and integral intensity K of the absorption band stretching vibration of the SH group for solutions of both mercaptans. In figure 1 are depicted absorption curves for solutions of propyl mercaptan in CCl_4.

The stretching vibration band of the SH group in spectra of pure mercaptans (molar concentration 13.5 and 11.2 moles/l. for ethyl and propyl mercaptans, respectively) have half widths in the vicinity of 58 cm^{-1}. On going to dilute solution in CCl_4 the band shifts in the direction of higher frequency by approximately 20 cm^{-1}, the half width diminishes to 25 cm^{-1}, but the integral intensity falls 7-8 fold. As is evident from figure 1, in the intermediate concentrations we succeeded in finding band splitting.

All these facts, of which most important are the band splitting and the strong diminution in its intensity, are certain evidence for the existence in liquid mercaptans of hydrogen bonding which leads to association of the molecules.

The 2564 cm^{-1} band in the spectra of pure mercaptans must be assigned to vibrations of the SH group, perturbed by hydrogen bonding, while the 2584 cm^{-1} band is assigned to the vibrations of the SH groups of monomeric mercaptan molecules in solution. The absence of SH band splitting in solutions of mercaptans in benzene, ascertained by Gordy and Stanford [13], might be explained, first of all, as due to bad dispersion caused by their use of a spectrometer with NaCl prisms, and secondly, as due to insufficient inertness of benzene as the solvent, since it is possible that complexes of mercaptans with benzene are formed [17].

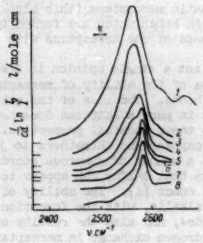

Figure 1. Absorption bands of the valence vibrations of the SH group in solutions of C_3H_7SH in CCl_4.

Concentration (moles/l.): 1 - 11.2, 2 - 7.7, 3 - 3.68, 4 - 2.69, 5 - 1.54, 6 - 0.1777, 7 - 0.134, 8 - 0.537.

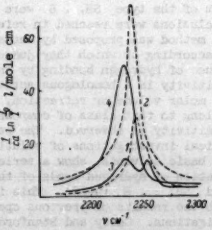

Figure 2. Absorption bands of the valence vibrations of the CD group of $CDCl_3$ in solutions.

1 - C_3H_7SH, 7.16 mole/l; 2 - C_3H_7SH, 0.727 mole/l; 3 - $(C_3H_7)_2S$, 8.56 mole/l; 4 - $(C_3H_7)_2S$, 0.980 mole/l.

The formation of association of mercaptan molecules ought to be accompanied by the appearance of the SH group perturbed in two ways- at hydrogen (the type -S-H. . . S) and at sulfur (type H . . .S-H). Under this circumstance the existence of rings of

dimers is considered unlikely due to geometrical considerations. For the most detailed study of the nature of the band at 2564 cm^{-1} it is of interest to examine spectroscopic evidence of the perturbation of each kind. Hence, we tried to realize each type of perturbation separately, using as solvents chloroform and dipropylsulfide.

On dissolving mercaptans in chloroform the latter ought to act as a proton donor. It ought to lead to formation of hydrogen bonding of the type

$$Cl_3CH\ldots S\langle^{H}_{R},$$

in other words, in dilute solutions of propyl mercaptan in chloroform one ought to expect the appearance only of the SH group perturbed at the sulfur atom. For verification of the supposition concerning the formation of a hydrogen bond between molecules of mercaptan on one hand, and molecules of chloroform on the other, spectra were taken of solutions of deuterochloroform, $CDCl_3$, in C_3H_7SH in the region of the absorption band of the stretching vibration of the group CD. The corresponding curves are presented in figure 2. In agreement with reference [20], $\nu(CD) = 2252$ cm^{-1} in spectra of pure liquid $CDCl_3$, while the integral absorption coefficient equals 250 l/mole. cm^{-2}. In a spectrum of solutions of $CDCl_3$ (7.16 mole/l.) in C_3H_7SH in the region of the CD stretching vibration two bands are found at 2243 and 2252 cm^{-1}, with the total integral absorption coefficient of both, K = 820 l/mole. cm^2. Upon diminishing the concentration of $CDCl_3$ to 0.727 mole/l only a single band at 2238.5 cm^{-1} remains in the spectrum, K = 1650 l/mole. cm^2. The splitting and increase in intensity of the CD band of the stretching vibration of $CDCl_3$ when dissolved in C_3H_7SH shows hydrogen bonds are really formed between molecules of the mercaptan and chloroform.

Table 2

Frequencies and intensities of the bands of valence vibrations of the SH group in spectra of solutions of C_3H_7SH

Solvent	Concentration (moles/l.)	ν(SH) (cm^{-1})	K (l./mole·cm^2)
CCl_4	0.0537	2583	120
$CHCl_3$	6.29	2566	430
	1.88	2586 *	390
	0.128	2588	120
	0.0895	2588	110
$(C_3H_7)_2S$	1.33	2552	770
$(CH_3)_2CO$	8.72	2566	840
	5.36	2570	1420
$(CH_2)_4O_2$	5.53	2567	840
$(C_2H_5)_3N$	8.07	2566 ~2460	810
	5.46	2563 ~2460	1200
	5.06	2560 ~2460	1230

* High frequency component of double bands.

In table 2 are presented data on the frequency and intensity of the valence SH band in the spectrum of C_3H_7SH dissolved in $CHCl_3$. On measuring dilute solutions the band is shifted in the direction of higher frequency, and the intensity diminishes, but bifurcation of the band is clearly evident at C = 1.88 moles/l. If it is assumed perturbation of the sulfhydryl group by hydrogen bonding at sulfur is approximately equivalent both in the case of the interaction between mercaptan molecules, and in the case of interaction between molecules of mercaptan and chloroform, then on the basis of the results obtained it is possible to reach the conclusion that such perturbation is not reflected to a noticeable extent in the band ν(SH). Hence, it follows appearance of the association band at 2564 cm^{-1} in spectra of aliphatic mercaptans is connected, basically, with perturbation of the sulfhydryl group at hydrogen. Based on the considerations cited, we can expect that parameters of the ν(SH) band in the spectrum of a dilute solution of the mercaptan in a thioether ought not to differ significantly from those parameters in the spectrum of pure mercaptan. In relation to the mercaptan the thioether ought to act as a proton acceptor, leading to formation of hydrogen bonding,

$$R - S - H\ldots S\langle^{R}_{R},$$

i. e. in a solution of a mercaptan in a thioether the sulfhydryl groups will be perturbed primarily at hydrogen, and, besides, to the same extent approximately as in the mercaptan itself.

In the spectrum of a solution of C_3H_7SH in dipropyl sulfide, $(C_3H_7)_2S$, as can be seen in table 2, the intensity of the SH band is really not changed, however some shift to a lower frequency occurred. In order to establish whether this was connected with the properties of the sulfur atom of the sulfide molecule, the influence of dipropylsulfide on the band of the stretching vibration of the CD group of $CDCl_3$ was studied. The corresponding curves are presented in figure 2. Splitting of the CD band into two bands, at 2252 and 2231 cm^{-1} is found in the spectrum of a solution of $CDCl_3$ (8.56 moles/l.) in $(C_3H_7)_2S$. In a less concentrated solution of $CDCl_3$ (0.98 m./l.) only the 2231 cm^{-1} band (K=1340 l/mole. cm^2) is retained. Consequently, in a solution of $CDCl_3$ in $(C_3H_7)_2S$ hydrogen bonding arises, for which, just as for SH bands, this is accompanied by a greater shift of the CD band than in the case of the bonding of deuterochloroform with mercaptans. It is of interest that in a similar way solution of $CDCl_3$ in (oxygen) alcohols and ethers affects the band ν(CD): under circumstances of formation of hydrogen bonding in solutions of $CDCl_3$ in ethers a greater shift of the CD frequency is found than in a spectrum of the solution in methanol [20, 21]. If the shift of the band upon formation of a complex really is characteristic of the electron donor ability of the atom-acceptor proton [22], then, on the basis of the results set forth, it is possible to assert that this ability in sulfur in the

R-S-H group is markedly less than in the R-S-R group.

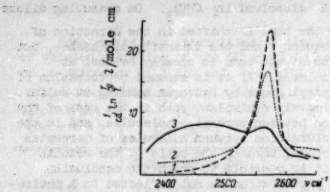

Figure 3. Absorption bands of the valence vibrations of the SH group in solutions of C_3H_7SH. 1 - $(CH_3)_2CO$, 5.36 mole/l; 2 - $(CH_2)_4O_2$, 5.53 mole/l; 3 - $(C_2H_5)_3N$, 5.46 mole l.

Investigation of solutions of C_3H_7SH in acetone, dioxane and triethylamine permits the determination of spectral characteristics of hydrogen bonding in these systems. The corresponding curves are presented in figure 3. Solution in oxygen containing solvents is accompanied by only a small drop in the frequency of the mercaptan ν(SH) band, the intensity of which is strongly increased under these conditions. On the contrary, upon dissolving propyl mercaptan in triethylamine, a significant shift takes place, as well as washing out of the SH band, being accompanied also by an increase in its intensity. A similar picture of the influence of oxygen and nitrogen-containing solvents on the stretching vibration band of the XH group was found earlier in the case of chloroform solutions [23].

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July 15, 1958

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Remark during proof-reading: After this article was sent to the printer, the article by A. A. Spurr and H. F. Ryers, J. Phys. Chem. 62, 425, (1958), appeared, which was devoted to the measurement of the intensity of the absorption band of SH in the IR spectra of mercaptans. The conclusion concerning the existence of hydrogen bonding of the type SH...S in aliphatic mercaptans arrived at in our work is in agreement with the data of the authors mentioned, however their interpretation of their results raises objections. Analysis of the question concerning the possible types of equilibria in mercaptans will be published at a later date.

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The Effect of Temperature and Ultraviolet Irradiation on Luminescence of the CdI_2-$MnCl_2$, CdI_2-$MnCl_2$-PbI_2 Phosphors

G. P. BALIN

Abstract: The present work is an investigation of the temperature quenching of phosphors with a stratified crystal lattice structure. The phosphors are CdI_2 containing $MnCl_2$ and PbI_2 at various concentrations as activators. The darkening of the phosphor produced by an ultraviolet irradiation of λ=365 mμ and the joint effect of ultraviolet irradiation and temperature are also studied. The investigation and the results refer to the red band (λ=675 mμ).

We showed earlier [1] that on protracted ultraviolet irradiation (λ=365 mμ) a phosphor of the type CdI_2-$MnCl_2$ darkens noticeably*, this being accompanied by a weakening of the luminescence proportional to the duration of irradiation. This phenomenon makes difficult the investigation of the temperature quenching of a given phosphor, since the weakening of the luminescence evoked by the ultraviolet irradiation is superimposed on this effect. As was also mentioned in [1], at low temperatures (-196° C) the phosphor CdI_2-$MnCl_2$ gives a very weak luminescence, where the red luminescence is absent. At room temperature there is only one very strong red luminescence (center of band λ=675 mμ), which becomes weak at high temperatures.

It was necessary to separate both these factors which influence the luminescence from each other and investigate separately the effect of both the temperature and ultraviolet irradiation of the red luminescence band λ=675 mμ.

The behavior of the darkening of the phosphor was investigated at 20° C during 60 minutes of continuous irradiation, after which the phosphor was kept in darkness at room temperature for 44 hours and its darkening was investigated again (Fig. 1). As is evident from the figure, during the time of irradiation the intensity of a fresh, nonirradiated phosphor decreases to approximately ½ its initial value; after 44 hours a partial reduction of the luminescence to about 60% of the original value takes place.

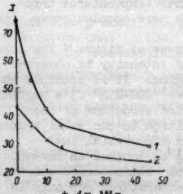

Figure 1. Decay of the luminescence intensity of the phosphor CdI_2+3%$MnCl_2$.
1 - not irradiated by ultraviolet light; 2-44 hrs.after irradiation.

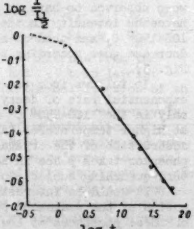

Figure 2. Decay of the luminescence intensity of the phosphor CdI_2+3%$MnCl_2$ on a logarithmic scale.

The new weakening of the luminescence is depicted by curve (2), which is almost parallel to the original curve (1).

Numerous measurements of the weakening of the luminescence on irradiation have shown that it has an hyperbolic character both for fresh and for previously exposed samples (Fig. 2).

The darkening of the following phosphors was also studied: CdI_2+1%$MnCl_2$, CdI_2+10%$MnCl_2$, CdI_2+20%$MnCl_2$, CdI_2+50%$MnCl_2$, CdI_2+3%$MnCl_2$+3%PbI_2, CdI_2+3%PbI_2.

The nature of the darkening for five of these phosphors is shown in figure 3.

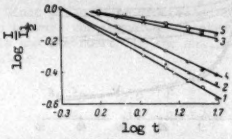

Figure 3. Decay of the luminescence intensity of irradiated phosphors at t=20° C.
1 - CdI_2+1%$MnCl_2$; 2 - CdI_2+3%$MnCl_2$;
3 - CdI_2+10%$MnCl_2$; 4 - CdI_2+3%$MnCl_2$+3%PbI_2;
5 - CdI_2+3%PbI_2.

Comparing the rate of the darkening of the phosphors CdI_2 with 1, 3, and 10% $MnCl_2$ (curves 1, 2, 3, in Fig. 3), we see that as the concentration of manganese chloride increases the drop in the intensity becomes less steep. Curves 4 and 5, figure 3, refer to phosphors in which lead iodide also serves as activator. As was pointed out in [1], the presence of PbI_2 causes the appearance of additional short wavelength bands. However, since the observation was made with the aid of an RG-1 filter, only the red band was investigated. Curve 5 shows that the phosphor with just the activator PbI_2 is hardly influenced by ultraviolet irradiation. It is possible that the red band of the phosphor with PBI_2 is different from the band of the one with the $MnCl_2$ activator. It was found that the phosphors CdI_2+20%$MnCl_2$, CdI_2+50%$MnCl_2$ darken slightly, i.e., actually the higher the manganese content, the weaker the influence of the ultraviolet irradiation. Thus, for example, the luminescence of the first of these phosphors weakens only by 10-15% after 10 minutes of irradiation, after which the weakening ceases.

To give any more or less exhaustive explanation of the observed weakening of intensity during ultraviolet irradiation is not possible for the present.

* For similar darkening of zinc sulphide phosphors, see, for example, the monograph of V. L. Levshin, "Fotoluminestsentsia zhidkikh i tverdykh veshchestv" (Photoluminescence of Liquid and Solid Substances), M., 1950, pp. 351-352.

One may, however, assert that since a recovery of the luminescence takes place with time, though it is not complete, then a purely chemical process must not be spoken of here. One may consider it proven that the red luminescence of the phosphor CdI_2+$MnCl_2$ is due to the presence of the manganese which, apparently, during the preparation of the phosphor occupies a cadmium lattice site, forming a mixed crystal. Then, evidently, during irradiation a photochemical process takes place under the influence of photons which leads to the disappearance of the luminescence center related to the manganese. It is characteristic that after protracted irradiation the color of the phosphor is changed in reflected light.

The fact that phosphors with large percentages of manganese chloride are relatively less influenced by ultraviolet irradiation apparently may be related to the temperature effect, namely: due to the thermal motion and a sufficient quantity of manganese ions, the latter rapidly regain that state in which they are capable of luminescing. The investigations we carried out on the temperature dependence of the weakening of the intensity of the phosphor (Fig. 4) advocate this position.

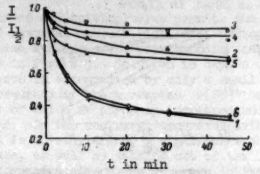

Figure 4. Decay of the luminescence intensity of the irradiated phosphor CdI_2+3%$MnCl_2$ at different temperatures.

1 - 20° C; 2 - 60° C; 3 - 100° C; 4 - 150° C; 5 - 200° C; 6 - 250° C.

As is evident from figure 4, on an increase of the temperature the quenching effect of the ultraviolet irradiation at first weakens and at 100° C practically disappears. Here the darkening of the phosphor can be barely observed. Then at still higher temperatures (150, 200 and 250° C) the influence of the irradiation again increases. As will be shown below, the temperature quenching also begins to have an effect at these temperatures.

In our opinion, the qualitative explanation of the concentration and temperature dependence of the effect of ultraviolet irradiation, may consist of the following.

In reference [1] it was established that if the phosphor is prepared only by simple mechanical grinding, as was done in [2], then the luminescence of the phosphor is very weak. In our case both compounds (or all three compounds in the case of three components) were first pulverized to a powder, then this mixture was fused and after rapid cooling again pulverized. It is well known that the essence of inserting an activator consists in the diffusion of the ions of the activator which, as is well known, is proportional to the temperature. It is evident that the best implantation of manganese ions in the lattice sites takes place during fusion. Apparently, ultraviolet irradiation leads to partial destruction of the luminescence centers connected with the manganese ions situated at the lattice sites. Thermal motion, on the other hand, again restores the previous state. Near 100° C these mutually opposed effects compensate each other, establishing the original active equilibrium. It was noticed that the recovery of the luminescence of the irradiated phosphor takes place much faster at high temperatures.

The temperature dependence of the luminescence of cadmium-manganese phosphors was also investigated. As was already pointed out, the red luminescence of the CdI_2+3%$MnCl_2$ phosphor vanishes completely at low temperatures, but becomes stronger on an increase in temperature. The maximum intensity of this luminescence is reached at 60° C, then it diminishes, and at 300° C the luminescence is approximately one-eleventh that at 60° C.

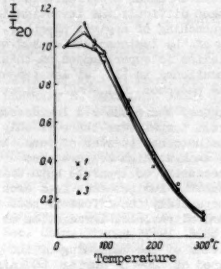

Figure 5. Temperature quenching.

1 - CdI_2+3%$MnCl_2$; 2 - CdI_2+10%$MnCl_2$; 3 - CdI_2 + + 50%$MnCl_2$.

The phosphors CdI_2+1%$MnCl_2$ and CdI_2+50%$MnCl_2$ also have the same temperature behavior (curves 1, 2, 3, Fig. 5). If the value of the intensity at 60° C is taken as the initial value, then all three phosphors were observed to have an almost linear drop in luminescence intensity in the interval from 60 to 100-150° C, and then at higher temperatures this decrease goes according to a more complex curve (see Fig. 5).

It follows from the curves of figure 5 that the exponential rate of decay of intensity is observed only in the 100-250° C region. It is possible that at higher temperatures (above 200-250° C) a partial destruction of the crystalline structure of the phosphor takes place in addition to the usual temperature quenching subject to an exponential law.

It would be interesting to conduct an investigation of the weakening of the luminescence intensity of these phosphors at low temperatures not only in the red band but also in other bands with lead iodide as an activator.

It is possible that the low luminescence intensity at higher manganese chloride concentrations is explained by the fact that since the absorption takes place in the lost phosphor, i. e., in the cadmium iodide, then for large $MnCl_2$ concentrations the absorption, hence also the radiation, will be weaker.

July 15,1958

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Dependence of Stored Light-Sums at Levels of Various Depths On the Excitation Density

IU. M. POPOV

Abstract: We consider a phosphor with two trap levels at different depths. It is assumed that from the trap levels electrons are ejected into the conduction band by thermal vibrations of the lattice. The probability of a thermal ejection from a trap level is expressed, according to the principle of detailed balancing, by the probability of capture in the same trap level. It is shown that in the stationary state the ratio of the number of electrons stored in the deep levels to the number stored in the shallow levels is proportional to the product of two factors, one of which represents the ratio of the total number of deep levels to the number of shallow levels, and the other decreases monotonically with an increase in the excitation intensity.

The storage of large light sums in a stationary state of photoluminescence, at the deeper trap levels under low excitation intensities has been observed in a number of experimental investigations [1, 2]. The filling of the shallower layers with an increase in excitation intensity leads in part to a well known effect in photo- and cathode- luminescence -- an increase in the extinction rate with an increase in excitation intensity.

In reference [2] it is assumed that the increased filling of the shallow layers accompanying an increase in excitation intensity is connected with the stimulated emission. It is doubtful, however, that at low intensities the stimulated emission turns out to have any real effect, especially an effect confined to the deep layers. It is shown in the present paper that under the usual assumptions on the kinetics of processes in phosphors with two trap levels it is unnecessary to bring in the stimulated emission to explain the rather strong dependence of the above mentioned ratio (of light sums stored in deep levels to light sums stored in shallow levels) on the excitation intensity.

Let us consider a phosphor with two types of trap levels (Fig. 1). We introduce the following notation: Q is the number of pairs of electrons and holes arising from internal excitation (proportional to the excitation intensity); N is the number of electrons in the conduction band; m is the number of holes; n_1, n_2 the numbers of electrons in the 1 and 2 levels, respectively; ν_1, ν_2 the number of levels of types 1 and 2; W_1, W_2 the transition probabilities for electrons from the conduction band to the 1 and 2 trap levels; p_1, p_2 the probabilities of thermal ejection of an electron from the 1 and 2 levels, respectively, and α is the probability of recombination of a conduction electron with a hole (radiative and non-radiative). All magnitudes are referred to 1 cm^3.

Let us write down the kinetic equations for the stationary case. For simplicity we shall assume that absorption takes place only in the activator levels, since the behavior of the holes is irrelevant to our conclusions. The system of equations has the following form:

(1)

$$\alpha Nm + W_1N(\nu_1 - n_1) + W_2N(\nu_2 - n_2) = Q + p_1n_1 + p_2n_2;$$

$$W_1N(\nu_1 - n_1) = p_1n_1;$$

$$W_2N(\nu_2 - \nu_2) = p_2n_2;$$

$$\alpha Nm = Q; \quad m = N + n_1 + n_2.$$

It is essential that we neglect the recombination of electrons in the trap levels with holes. This neglect is fully justified by the absence of holes in the valence band. In case the number of electrons recombining with holes in the trap levels is small compared to the number emitted from the conduction band our assumption is also valid. We obtain from equations (1)

(2)
$$n_1 = \frac{W_1\nu_1N}{p_1 + W_1N}, \qquad n_2 = \frac{W_2\nu_2N}{p_2 + W_2N}.$$

Since we shall be interested later only in the ratio between the number of electrons in the deep levels and the number in the shallow levels, we calculate

(3)
$$\frac{n_2}{n_1} = \frac{W_2\nu_2}{W_1\nu_1} \cdot \frac{p_1 + W_1N}{p_2 + W_2N}.$$

In the discussion later we shall employ the principle of detailed balancing to express the probability of thermal emission in terms of the probability of transition from the conduction band to the appropriate level. This operation allows us to eliminate from (3) all probabilities, which are as a rule unknown.

We consider a trap level with ν electrons (Fig. 2) in thermal equilibrium with the conduction band (at a temperature $T = 0$ there are no free electrons in the band -- they are all in the trap levels). The number of electrons in the conduction band at temperature T is given by

(4)
$$n_e = \int_{E_2}^{\infty} w_e(E)\, \rho(E)\, dE = N_{eff} \exp\left[-\frac{E_2 - \mu}{kT}\right].$$

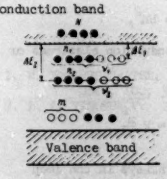

Figure 1

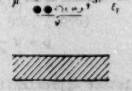

Figure 2

The probability that an electron will be found in a level with energy E is

$$w_e(E) = \frac{1}{\exp\left[\frac{E-\mu}{kT}\right]+1} \approx \exp\left[-\frac{E-\mu}{kT}\right],$$

and the density of this state in the conduction band is

$$\rho(E)\,dE = \frac{2\cdot 4\pi P^2 dP}{h^3} = 2\cdot 4\pi \left(\frac{2m^*}{h^2}\right)^{\frac{3}{2}} (E-E_2)^{\frac{1}{2}}\,dE.$$

In these expressions E_2 is the energy of the lowest region of the conduction band; m^* is the effective mass of a conduction electron; μ is the value of the chemical potential. Then

$$N_{eff} = \frac{2(2\pi m^* kT)^{3/2}}{h^3} = 4.82\cdot 10^{15}\left(\frac{m^*}{m}T\right)^{3/2}. \tag{5}$$

The probability of observing a hole in the level E is

$$w_h(E) = 1 - w_e(E) = \frac{1}{\exp\left[\frac{\mu-E}{kT}\right]+1} \approx \exp\left[-\frac{\mu-E}{kT}\right].$$

The total number of holes in a trap level with energy E_1 is

$$n_h = \nu \exp\left[-\frac{\mu-E_1}{kT}\right].$$

From the equality $n_h = n_e$ we obtain

$$\exp\left[\frac{\mu}{kT}\right] = \sqrt{\frac{\nu}{N_{eff}}}\exp\left[\frac{E_1+E_2}{2kT}\right].$$

The equilibrium number of electrons is

$$n_e = \sqrt{\nu N_{eff}}\exp\left[-\frac{\Delta E}{2kT}\right] \tag{6}$$

(ΔE is the depth of the trap level).

On the other hand, using the notation developed at the beginning of the paper, we have from the thermodynamic equilibrium of the trap level and the conduction band

$$p(\nu - n) = Wn^2, \tag{7}$$

where n is the number of conduction electrons or holes in the trap level.

We obtain from (7)

$$p = W\frac{n^2}{\nu - n} \approx W\frac{n^2}{\nu}. \tag{8}$$

This latter approximation is always in the deep levels where $\Delta E > kT$. Substituting in (8) the expression (6) for the equilibrium number of electrons, we find the relation between p and W

$$p = WN_{eff}\exp\left[-\frac{\Delta E}{kT}\right]. \tag{9}$$

Equation (9) was derived for the case when a trap level of one type is present. If we neglect the interaction between impurities yielding trap levels of different depths, the addition of a trap level of a second type does not affect the probabilities W_1 and P_1 connected with a level of the first type, and conversely. Accordingly, equation (9) holds individually for each type of trap level, although μ and n_e will not be defined by the formulas given above.

We have further

$$p_1 = W_1 N_{eff}\exp\left[-\frac{\Delta E_1}{kT}\right]; \tag{10}$$

$$p_2 = W_2 N_{eff}\exp\left[-\frac{\Delta E_2}{kT}\right].$$

Substituting (10) in (3) we obtain

$$\frac{n_2}{n_1} = \frac{\nu_2}{\nu_1}\cdot\frac{N_{eff}\exp\left[-\frac{\Delta E_1}{kT}\right]+N}{N_{eff}\exp\left[-\frac{\Delta E_2}{kT}\right]+N}. \tag{11}$$

Equation (11) is free of undetermined probabilities, and its behavior with respect to dependence on the excitation level can be easily analyzed. It is clear that the only quantity in (11) that depends on the excitation intensity is the number N of electrons in the conduction band. N itself can be found by solving the system of equations (1). We shall not carry out the solution, however, since this would again involve us in difficulties with undetermined probabilities, for example, α. We shall consider only a very general dependence of N on Q, namely a monotonic increase in N with increase in the excitation intensity, which leads to a monotonic decrease in the ratio $n_2:n_1$. The latter dependence is obvious, since in (11) only the second factor changes with an increase in the excitation intensity and $\exp\left[-\frac{\Delta E_1}{kT}\right] > \exp\left[-\frac{\Delta E_2}{kT}\right]$ (by hypothesis, the second level is deeper than the first), so that $N(Q)$ reaches the value $N_{eff}\exp\left[-\frac{\Delta E_2}{kT}\right]$ before it reaches $N_{eff}\exp\left[-\frac{\Delta E_1}{kT}\right]$.

At low excitation intensities, when

$$N < N_{eff}\exp\left[-\frac{\Delta E_2}{kT}\right], \tag{12}$$

we find

$$\frac{n_2}{n_1} = \frac{\nu_2}{\nu_1}\exp\left[\frac{\Delta E_2 - \Delta E_1}{kT}\right]. \tag{13}$$

It follows from (13) that at low excitation densities, when (12) is satisfied, there can be three different cases of storage, depending on the ratio $\frac{\nu_2}{\nu_1}$.

Case 1

(14) $$\nu_2 \gg \nu_1, \text{ or } \nu_2 < \nu_1 \text{ but } \nu_2 \exp[-\frac{\Delta E_2 - \Delta E_1}{kT}] > \nu_1.$$

In this case

$$n_2 : n_1 > 1,$$

that is, the number of electrons stored in the deep levels is equal to the number stored in the shallow levels.

Case 2

(15) $$\nu_2 < \nu_1, \quad \nu_2 \exp[\frac{\Delta E_2 - \Delta E_1}{kT}] \approx \nu_1$$

and

$$n_2 : n_1 \approx 1,$$

that is, the number of electrons stored in the deep levels is greater than the number stored in the shallow levels.

Case 3

(16) $$\nu_1 > \nu_2 \text{ and } \nu_2 \exp[\frac{\Delta E_2 - \Delta E_1}{kT}] < \nu_1$$

$$n_2 : n_1 < 1.$$

The absolute number of electrons stored in the deep levels is in this case less than the number stored in the shallow levels. Since in all three cases the ratio $n_2 : n_1$ decreases with an increase in the excitation intensity, which follows from (11), the absolute increase in the number of electrons in the shallow levels is greater than the absolute growth in the number of electrons in the deep levels in cases 2 and 3, as the excitation intensity increases. In case 1 we cannot conclude that the absolute growth in the number of electrons in the shallow levels is necessarily greater than that in the deep levels, since in this case the ratio $n_2 : n_1$ can decrease independently of the absolute rates of increase.

At high intensities of the exciting illumination, when, $N > N_{eff} \exp[-\frac{\Delta E_1}{kT}]$ it follows from (11) that

(17) $$\frac{n_2}{n_1} = \frac{\nu_2}{\nu_1} = \text{const.}$$

But in this case it is necessary to take into account the effect of stimulated emission and of a number of processes connected with the high densities of conduction electrons and holes, which were neglected in the derivation of (11) and (17).

The results we have obtained give rise to the possibility of experimentally determining the ratio of the total number of deep levels, when the depths are known, in terms of the ratio of stored light sums, using low intensities of excitation, so that (13) is valid. We have carried out the derivation for levels at two different depths. Similar results can be easily obtained for a large number of different levels, since all calculations, for example for level 3, coincide precisely with those carried out above, and the final results for the ratio $n_3 : n_1$ can be obtained by substituting the subscript 3 for the subscript 2 throughout.

We must again emphasize the fact that in deriving the above relationships we made two fundamental assumptions: 1) the capture and emission of electrons by a trap level arises from thermal vibrations of the lattice; 2) there are no direct transitions of electrons from the trapping levels to holes in the valence band.

In our opinion, the first assumption is generally valid, since the probability of non-radiative capture of an electron in a deep level (and a fortiori in a shallow level) is as a rule 10 times greater than the probability of capture with emission of photons. Accordingly, the latter can be neglected in comparison with the former, which is what we have done in the present derivation. Generally speaking, also, we can by a similar method express the probability of radiative recombination in terms of the probability that a photon will eject an electron from the trap level into the conduction band.

As indicated above, the second assumption is valid when there are no holes in the valence band (excitation occurs only in the activator levels, of which the height above the top of the valence band is large compared to kT.) All the rules derived by us remain in force if the probability of transition from trap level to a hole in the valence band is small, or if the number of photon emissions per second from the trap level to the conduction band is much larger than the number of transitions from this level to the valence band. This is always the case at low excitation intensities, when the number of holes in the valence band is small.

In conclusion I must record my gratitude to Professor V. L. Levshin for his interest in the work and a number of valuable observations.

May 12, 1958

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The Influence of Non-Radiative Recombination, on Saturation during Cathodoluminescence *

IU. M. POPOV AND V. P. SHABANSKII

Abstract: Kinetic equations applicable to problems of luminescence are solved for a number of particles in the conduction band and trapping levels. These equations include triple recombination processes, which are important for large densities of free charge carriers. Included in triple recombination is the process of the ionization of electrons from traps by conduction electrons or holes.

It is shown that precisely such densities of free electrons and holes correspond to the nonlinear part of the yield of cathodoluminescence, which appears at sufficiently strong irradiation levels. Numerical estimates and the form- of the dependence of the yield on the intensity of irradiation correspond to experiment. The energy balance for electrons in the recombination processes is formulated, and an estimate given of the electron temperature.

In cathodoluminescence a crystal phosphor is excited by a stream of electrons. This is responsible for the special nature of cathodoluminescence, which distinguishes it from photo-luminescence. The difference consists primarily in the fact that, for the same surface density of excitation radiation, there is a much greater intensity of volume excitation in cathodoluminescence. This takes place because the electrons do not penetrate deeply into the luminophor and the excitation is concentrated in a thinner surface layer than is true for the case of excitation by light; this is true regardless of the fact that the energy of the electrons may be many times larger than the ionization energy of the luminescence centers, so that they may not only cause multiple ionization, but also form electron avalanches. The electrons, in contrast to quanta, fail to penetrate into the crystal not because their cross-section for ionization is greater than for photons, but chiefly because of scattering by phonons during which the electrons give up a considerable part of their momentum and an insignificant amount of energy. The length of the path over which a thermal electron completely loses its momentum is of order 10^{-6} cm. Therefore an energetic excited electron loses its directed momentum by phonon scattering at a depth of 10^{-5} -10^{-4}cm. The fact that during this process the electron loses but little of its energy explains the relatively high quantum yield of cathodoluminescence.

The laws of cathodo- and photo-luminescence seem to differ but little from each other when they have the same density of volume excitation [1].

The fundamental nature of cathodoluminescence appears at high volume densities of excitation, which cannot be achieved in photo -luminescence. One of the characteristics of stationary excitation is that for large excitation densities the linear dependence of the emission intensity on increasing excitation intensity goes over into a nonlinear dependence; and a tendency appears for the luminescence to saturate. If this phenomenon is due only to the increase in the number of excited electrons and holes and not to some sort of accessory factor (for example, a heating up of the crystal phosphor, leading to an increase in the probability of non-radiative transitions), then this means that for large excitation concentrations a new mechanism for non-radiative transitions comes into play, which depends on the excitation concentration in a different way than the usual non-radiative "thermal" recombination. This mechanism might be triple recombination, i.e. a process which is the inverse of impact ionization. During such a process one of the two electrons colliding in the presence of a vacant level recombines, giving energy to the other electron. Another possibility is that the electron recombines, colliding in the presence of a vacant level with a free hole in the valence band and gives energy to the hole. The same may be said for the recombination of holes at levels occupied by electrons. We include these processes in the kinetic equations for equilibrium of excitation and recombination in the usual energy model of a crystal phosphor containing ν_1 donors (or trapping levels), located at a distance Δ_{12} below the bottom of the conduction band and n_1 acceptors (or luminescence centers) at a distance Δ_{34} above

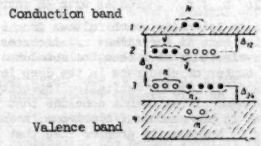

Figure 1

Explanation in text

the valence band (figure 1). The conduction band, trapping levels, luminescence centers and the valence band are designated by the indices 1,2,3,4, respectively. In figure 1, N is the number of free electrons in the conduction band (1), ν is the number of electrons in the trapping levels (2), n is the number of holes in the activator levels (3), and m is the number of holes in the valence band (4).

We designate the probability for radiative recombination of electrons and holes from band i to level j by W_{ij}, and the probability for a non-radiative thermal recombination by W^{β}_{ij}; the total probability, which is linearly dependent on concentration, has two parts: $W_{ij} = \tilde{W}_{ij} + W^{\beta}_{ij}$. Recombination from band to band will not be considered, nor will transitions of the sort 2-3. The probability

* Presented at the VII Conference on Luminescence

of triple recombination during the collision of two electrons, two holes, or a hole with an electron will be designated by W_{ij}^{ee}, W_{ij}^{hh}, or W_{ij}^{eh}, respectively. Finally we indicate the probability for thermal ionization by p_{ij}, the intensity of external irradiation per square centimeter by I, the ionization cross-section by κ_{ij}, the number of atoms of the host material by n_a, and we write the system of kinetic equations which determine N, ν, n, m, in the form

(1)

$$\frac{\partial N}{\partial t} = I[\kappa_{14}n_a+\kappa_{21}\nu+\kappa_{31}(n_1-n)]+p_{12}\nu-W_{12}N(\nu_1-\nu)-W_{13}Nn-$$

$$-W_{12}^{ee}N^2(\nu_1-\nu)-W_{12}^{eh}Nm(\nu_1-\nu)-W_{13}^{ee}Nn^2-W_{13}^{eh}Nmn,$$

$$\frac{\partial \nu}{\partial t} = -I\kappa_{12}\nu + I\kappa_{42}(\nu_1-\nu)-p_{12}\nu + W_{12}N(\nu_1-\nu)-W_{24}\nu m +$$

(2) $$+W_{12}^{ee}N^2(\nu_1-\nu)+W_{12}^{eh}Nm(\nu_1-\nu)-W_{24}^{hh}m^2\nu - W_{24}^{eh}mN\nu,$$

$$\frac{\partial n}{\partial t} = -I\kappa_{34}n +I\kappa_{31}(n_1-n)-p_{34}n+W_{34}m(n_1-n)-W_{13}Nn +$$

(3) $$+W_{34}^{hh}m^2(n_1-n)+W_{34}^{eh}mN(n_1-n)-W_{13}^{ee}N^2n-W_{13}^{eh}mNn,$$

(4) $$N + \nu = n + m.$$

The first term in equation (1) is the basic one, which describes excitation from band to band; so that the number of electrons appearing in the conduction band per unit time per unit volume $Q=I\kappa_{14}N_a$ is determined primarily by this term. In considering this term we will neglect the second and third terms, which describe the emissive action of the light and excitation from the activator levels. The corresponding terms in equations (2) and (3) are also small and will be neglected when they appear in combination with the term $I\kappa n_a$**.

Combining equations (1) and (2) we find for the stationary case

(5) $$W_{13}Nn=Q-W_{24}\nu m-W_{13}^{ee}N^2n-W_{13}^{eh}Nmn-W_{24}^{hh}m^2\nu-W_{24}^{eh}Nm\nu,$$

where $Q=I\kappa_{14}n_a$. The intensity of the emission is

(6) $$Q_{em.} = \tilde{W}_{13}Nn = ZW_{13}Nn$$

where $Z = \tilde{W}_{13}/W_{13}$ is the quantum yield. Usually the nonlinear character of the dependence of Q_{em} on Q is explained by the more intense non-radiative recombination (W_{24}) of electrons from trapping centers with holes in the valence band as compared with the recombination (W_{13}). The nonlinearity occurs when the second term on the right of equation (5) begins to be of the same order of magnitude as the left hand side of the equation. However since we are dealing with phosphors where the linear dependence of the emission intensity on excitation extends to large values of Q, the above indicated case does not obtain. Hence the nonlinearity can only occur when some other one of the remaining terms on the right side of equation (5), describing triple recombination, becomes of the same order as the left member.

For a numerical estimate of the quantity Q, for which the nonlinear behavior begins, it is necessary to know the transition probabilities W_{ij}, p_{ij}, W_{ij}^{ee} etc., appearing in the equation.

The probabilities for radiative transitions may be taken from reference [3] where they were derived assuming a hydrogenic model for the

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** The reverse process from triple recombination, viz.impurity ionization, is not taken into account in equations (1-4). At the end of the present article and in reference [2] it is shown for the stationary state in cathodoluminescence that the distribution of conduction electrons may be considered to be Maxwellian with a temperature $T_{eff.}$ which is near the temperature of the lattice T (estimates of these temperatures are given). Hence the number of impurity ionizations due to fast electrons may be neglected in comparison with thermal ionization and triple recombination, in which the slow electrons and holes take part. During triple recombination the electron which receives energy rapidly loses it because of collisions with the lattice (the concentration of impurity atoms is much smaller than the number of atoms of the host); this continues until the energy $\epsilon \approx kT_{eff.}$ and the electron may no longer ionize ($kT_{eff.}$ is in our case considerably smaller than the depth of the shallowest trapping level). It is necessary to take account of ionization in the presence of an electric field, when $kT_{eff.} \approx \Delta_{12}$, as is shown in a paper of one of the authors [3]. We point out also that usually when taking account of the excitation effect of light, described by the term $I\kappa_{31}(n_1-n)$ which enters the first and third equations, it is usually forgotten that there is an excitation of equal importance which is described by the term $I\kappa_{42}(\nu_1-\nu)$ which enters the second equation. This term takes account of electron transitions from the valence band to a trapping level (or the transition of a hole from a trapping level into the filled valence band) as a consequence of the action of light or of electrons. Similarly, in addition to the emissive action of light on electrons in trapping levels ($I\kappa_{21}\nu$), it is necessary to take account also of the equally important effect of light which transfers holes from activator levels into the valence band (term $I\kappa_{34}n$ in the third equation).

impurity in a semiconductor. In the same paper this model was used to compute the triple recombination probability W_{ij}^{ee}. Expressions for W_{ij}^{ee} having a slightly different form but coinciding in order of magnitude were derived in reference [4]. However in this latter paper the triple recombination probability W_{ij}^{eh}, describing the fall of a thermal electron into a thermal hole with the ejection of an impurity electron into the conduction band, turned out to be four orders of magnitude larger than W_{ij}^{ee}. (This turned out to be large enough to allow the author to explain nonradiative recombination in pure germanium.) This result seems surprising since it has no physical basis (the author introduces none; the result is purely mathematical) by which to distinguish in a given case between the interaction of two electrons, and of an electron and a hole. It seems that the anomalously large value of W_{ij}^{eh} in reference [4] was obtained by the use of a hole wave function as the function to describe an electron in the valence band. This can lead to an incorrect order of magnitude of these quantities, since in this case the wave functions of an electron in the conduction band and the valence band for a given momentum are not orthogonal (this was the case considered in reference [4]).

For the transition probabilities we shall use the results of reference [3] (cf. formulae (2,4), (2,6), (2,22) and (2,23), in which photo-recombination was designated by β, and triple recombination by β'). We then have

$$(7)\quad \tilde{W}_{ij} = \frac{2\kappa_H \eta^2 \Delta_{ij}^2}{c\, m\sqrt{2\,\pi m k T}} \left(\frac{E_R}{\Delta_{ij}}\right)^{3/4} \left(\frac{m}{m^*}\right)^{11/4}$$

$$(8)\quad \tilde{p}_{ij} = \tilde{W}_{ij} 2 \left(\frac{2\pi m^* k T}{h^2}\right)^{3/2} \exp\left[-\frac{\Delta_{ij}}{kT}\right],$$

$$(9)\quad W_{ij}^{ee} = \frac{2 q_{max}^2 h^3}{(\pi m)^2 kT} \frac{E_R}{\Delta_{ij}} \left(\frac{m}{m^*}\right)^3$$

where κ_H is the resonance cross-section for the ionization of hydrogen, η is the index of refraction at the frequency of the transition being studied, c is the velocity of light, m^* is the effective mass, and m is the actual mass of the electrons, k is the Boltzmann constant, T is the temperature, E_R is the Rydberg energy, h is Planck's constant, q_{max} is the maximum cross-section for the ionization of hydrogen by an electron.

One must point out that the hydrogen model is more valid for transitions between nearby levels than between distant levels. However, since we are interested only in order of magnitudes, it is possible to use it, with appropriate restrictions, to estimate the transitions to Δ_{13}, Δ_{24}.

From (7)-(9) it is clear for example that $\tilde{W}_{13}/\tilde{W}_{12} = (\Delta_{13}/\Delta_{12})^{5/4}$ at the same time that $W_{13}^{ee}/W_{12}^{ee} = \Delta_{12}/\Delta_{13}$, i.e. the probability of triple recombination decreases with the depth of the levels. (For the case of our estimate, in agreement with reference [4], $W_{13}^{ee}/W_{12}^{ee} = (\Delta_{12}/\Delta_{13})^3$).

For $\Delta_{12}=\Delta_{34}\approx 0.3$ev., $\Delta_{13}=\Delta_{24}\approx 2.7$ev., $m^*\approx m$, $T=300^\circ$K then in order of magnitude

$$\tilde{W}_{12}=\tilde{W}_{34}\approx 10^{-12}\,\mathrm{cm}^3\mathrm{sec}^{-1},\quad \tilde{W}_{13}=\tilde{W}_{24}\approx 10^{-12}\,\mathrm{cm}^3\mathrm{sec}^{-1},$$

$$W_{12}^{ee}=W_{34}^{hh}\approx 10^{-27}\,\mathrm{cm}^6\mathrm{sec}^{-1},$$

$$W_{13}^{ee}=W_{24}^{hh}\approx 2\cdot 10^{-29}\,\mathrm{cm}^6\mathrm{sec}^{-1};\quad \tilde{p}_{12}\approx 10^2\,\mathrm{sec}.^{-1}$$

Unfortunately we are not able to say anything about the importance of non-radiative thermal recombination. However its order of magnitude may be compared with the order of the radiative recombination using the quantum yield. If we take the quantum yield $Z\approx 1/10$, then $W_{13}\approx 10^{-11}$.

We will solve the system of equations for the case of symmetrically arranged levels considered above, since to analyze the equations in the general case is extremely difficult. We assume also that $\nu_1 = n_1 \gg 10^{10}$. In this case equations (3) and (4) give $m=N$, $n=\nu$, which is obvious from considerations of symmetry. Equation (5) goes over into the equation

$$(10)\quad \nu = \frac{Q}{2(W_{13}+2W_{13}^{ee}N)N};$$

and the intensity of the emission is now equal to

$$(11)\quad Q_{em} = 2ZW_{13}N\nu = Z\,\frac{Q}{(1+2W_{13}^{ee}/W_{13}N)}$$

From equation (11) one may say immediately for what N there will be a linear dependence of Q_{em} on Q; viz. this will occur when

$$(12)\quad N=N_k \approx \frac{1}{2}\,\frac{W_{13}}{W_{13}^{ee}}$$

For the values assumed above $N_k \approx 2.5\cdot 10^{17}$.

In order to determine the dependence of N on Q it is necessary to solve the system of equations (1-4). Taking m=N and n=ν, and putting (10) into equation (1), we get an equation of the fourth order

$$(13)\quad aN^4 + bN^3 + cN^2 + dN + e = 0,$$

where $a = 8W_{12}^{ee}W_{13}^{ee}\nu_1$; $b = 4(W_{12}^{ee}W_{13}+W_{12}W_{13}^{ee})\nu_1$;

$$c = 2\nu_1 W_{12}W_{13} - 2QW_{12}^{ee} - 2QW_{13}^{ee};\quad d = -Q(W_{12}+W_{13});$$

$$e = -P_{12}Q.$$

This equation reduces to a quadratic and may be solved when N is much smaller than the magnitude given in (12) i.e. the equation is governed not by the criterion $N<N_k$, but by other parameters. This region however is uninteresting since we already know that it is the linear region, and the dependence of N on Q is of no interest in itself.

For $N > N_k$, equation (13) may be converted to a quadratic if the following condition is fulfilled:

$$(14) \qquad Q > \frac{W_{12}W_{13}\nu_1}{W_{12}^{ee}} \approx \frac{W_{13}^2\nu_1}{10^2 W_{13}^{ee}}$$

As we will see below this condition is fulfilled automatically. Then equation (13) goes into the equation

$$8W_{12}^{ee}W_{13}^{ee}\nu_1 N^2 = 2W_{12}^{ee}Q,$$

which gives

$$(15) \qquad N = \frac{1}{2}\sqrt{\frac{Q}{W_{13}^{ee}\nu_1}}$$

With the help of this expression and equation (10) we find

$$(16) \qquad Q = 2W_{13}\sqrt{\frac{Q\nu_1}{W_{13}^{ee}}}$$

To find the value of Q for which the deviation from linearity begins we put the value (12) for N_k into (15) (or extrapolating Q_{em} according to formula (16) from the linear region $Q_{em} = ZQ$):

$$(17) \qquad Q_k = \frac{W_{13}^2\nu_1}{W_{13}^{ee}}$$

Hence it is clear that the conditions $N > N_k$ and $Q > Q_k$ are considerably stronger requirements than (14), which we required for the solution of the equations. If we put into (17) the values which we assumed for the transition probabilities and for ν_1, we see that $Q_k \approx 10^{24}$ particles/cm^3. sec. and that $Q_{em.} \approx 10^{23}$ quanta/ cm^3. sec..

The determination of the exact form of the dependence of Q_{em} on Q in the neighborhood of Q_k may be carried out by numerical solution of equation (13), from which for a given Q we can locate the corresponding values of N and thence determine Q_{em}; from formula (11). The corresponding values are given below and in figure 2.

Q	N
10^{22}	$7.1 \cdot 10^{14}$
10^{23}	$0.58 \cdot 10^{16}$
10^{24}	$0.5 \cdot 10^{17}$
10^{25}	$0.25 \cdot 10^{18}$
10^{26}	10^{18}
10^{27}	$0.35 \cdot 10^{19}$
10^{28}	$1.1 \cdot 10^{19}$

The experimental data on the dependence of the cathodo-luminescent emission on the excitation density [5] show a deviation from linearity. According to the data of reference [5] the deviation from linearity begins for an electron beam of 50keV energy and current density $J \approx 10^{-1}$ amp./cm^2. In this case the penetration depth l is estimated in references [5] and [6] to be of the order of 10^{-3} cm. Assuming that one-tenth of all the incident electrons go into ionization we find that

$$Q \approx \frac{1}{10}\frac{JV}{l\Delta_{14}} \approx 10^{24}\frac{1}{\text{cm}^3\ \text{sec.}}$$

where Δ_{14} is the ionization energy.

Not only does Q_k agree well with the values obtained by us but also the form of the dependence of Q_{em} on Q coincides with the curve shown in figure 2. We agree with the discussion of the author of reference [5] concerning the deviation from a linear dependence of Q_{em} on Q which was found by earlier authors at lower excitation densities, and explained as being due primarily to a heating of the lattice. In reference [5] heating was prevented by applying the excitation in short pulses.

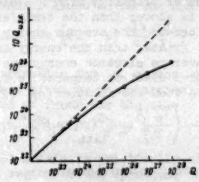

Figure 2

Curve of the derived theroretical dependence of Q_{em} on Q.

As has already been pointed out, during triple recombination the recombination energy is given to one of the interacting electrons (or holes). This electron rapidly loses its energy to phonons so that in the last analysis the energy is given to the lattice, as in the case of non-radiative thermal transitions. In addition, high energy electrons are ionized from the lowest band by the external beam. Those electrons whose energy is sufficient to form secondary electrons give their energy up in ionization. The avalanche process will proceed as long as the ionization energy for an electron is not less than the ionization energy $\Delta_{14} \approx \Delta_{13}$. Neglecting that part of the energy which the electrons give to phonons during the avalanche process and considering only the energy transfer to the lattice from the last electron in the avalanche, whose energy is less than Δ_{13}, we find that the total energy transferred to the lattice is *

*In the case of photoionization the energy received by the electrons may be determined exactly. It is equal to $Q(h\nu_0 - \Delta_{14})$, where ν_0 is the frequency of the incident light.

(18)
$$q_{latt}=\Delta_{13}Q+2w\Delta_{13}(W^{s}_{13}+2W^{ee}_{13}N)N+2(\nu_1-\nu)\Delta_{12}(W^{s}_{12}+2W^{ee}_{12}N)N.$$

The energy which goes into radiation is equal to

(19) $$q_{em}=2\tilde{W}_{13}\Delta_{13}N\nu+2\tilde{W}_{12}\Delta_{12}N(\nu_1-\nu).$$

As may be seen from formulae (10) and (15), with increasing N the number $\nu\to\nu_1$, so that transitions take place only between a band and the level which is farthest from it. In this region the latter terms in (18) and (19) may be neglected; then taking account of (15) we find

(20) $$\frac{q_{latt}}{q_{em}}=\frac{1}{Z}\left(1+\frac{2}{W_{13}}\sqrt{\frac{QW^{ee}_{13}}{\nu_1}}\right)$$

Hence it is clear that for $Q\approx Q_k$ this ratio grows by a factor of two and continues to increase as Q increases.

The transfer of energy from the electrons to the phonons is slower than the transfer of momentum. This occurs because the average energy of the electrons is greater than the energy of the lattice. Using this average electron energy one may speak of an effective electron temperature T_e which may be determined from the relation (cf. (2,3) in ref. [3]):

$$AN\frac{T_e-T}{T}\left(\frac{T_e}{T}\right)^{\frac{1}{2}}=q'_{latt}=(4\nu_1N^2W^{ee}_{13}+Q)\Delta_{13}=8\nu_1N^2W^{ee}_{13}\Delta_{13}.$$

For atomic semiconductors

$$A=\frac{16m^*v_s^2}{l}\sqrt{\frac{kT}{2m}},$$

where v_s - is the velocity of sound in the semiconductor, and l - is the electron mean free path. For $v_s\approx10^5$, $m^*\approx m$, $l\approx10^{-6}$, and $T\approx300^0$K., we find $A\approx5.10^{-4}$. In the expression for q'_{latt}, as distinct from q_{latt}, the non-radiative recombination did not enter since for this type of recombination the electron will completely give up its energy without any delay.

For $N\approx N_k$

$$\frac{T_e-T}{T}\left(\frac{T_e}{T}\right)^{\frac{1}{2}}\approx\frac{4\nu_1W_{13}\Delta_{13}}{A}$$

Then inserting the values assumed above for the parameters we see that for the transition to the nonlinear region $(T_e-T)/T\approx1$.

Increasing the electron temperature will lead to a change in the expression for the recombination probability. However at the beginning of the nonlinear region, where the electron temperature does not greatly exceed the lattice temperature T, the recombination coefficients do not change markedly, since according to reference [3] (see formulae (2,4), (2,6)) these coefficients do not depend strongly on T_e, viz.

$\tilde{W}(T_e)\sim\tilde{W}\sqrt{\frac{T}{T_e}}$, and $W^{ee}(T_e)=\frac{W^{ee}T}{T_e}$. Hence an increase in the electron temperature need not be considered in the calculation; and our estimate should remain valid.

In conclusion the authors extend their deep thanks to V. L. Levshin for his interest in this work and to M. V. Fok for a number of helpful comments.

May 12, 1958

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The Anomalous Skin-Effect and Optical Constants of Copper, Silver, Gold, and Nickel in the Infrared Region of the Spectrum

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Abstract: From the values of the optical constants of copper, gold, silver, and nickel which were measured previously [1,2] the concentration of conduction electrons N, the relaxation time τ, and the product of the speed at the Fermi[level]and the diffusion coefficient (1-p) were calculated on the basis of a theory of the anomalous skin effect. The calculations were carried out under the assumption that the conductivity of thick metallic layers precipitated in vacuum have a conductivity equal to that of the bulk metal.

Recently [1,2] we presented measurements of the optical constants of copper, silver, gold, and nickel in the infrared region of the spectrum; the results of the measurements were interpreted from the point of view of Drude's classical theory of free electrons. From the values we found of the optical constants of these metals the concentration of conduction electrons N, the relaxation time τ, and the static conductivity σ were determined. The latter turned out to be significantly below the conductivity measured on bulk samples by direct currents. An attempt to explain this discrepancy by defects in the surfaces, and consequently, an increase in the resistivity of the layers close to the surface in comparison with thick metals is not satisfactory.

The thing is, obviously, that Drude's dispersion formula is correct for the case of the normal skin effect, when the inequality $l \ll \delta$, is satisfied, where l is the free path length of the electrons, and δ is the skin depth. The current and the polarization at every point of the metal are determined by the simultaneous value of the field at each point, so long as the latter changes very slightly with distance over the length of the free path of an electron. For good conductors at room temperature thefree path length of an electron may be of the order of the skin depth, however at low temperatures the free path length increases significantly and the relation $l \gg \delta$ is satisfied; that is, anomalous skin effect occurs. In this case the field changes significantly in a distance of the mean free path and the current and polarization at a given point of the metal are determined by the field not only at that point, but by the rest of its environment. In other words, a point by point dependence between the current and the field does not exist. The amplitude of the waves as they penetrate into the metal does not decrease exponentially, as in the case of the normal skin effect, but in a more complicated manner, but nevertheless sufficiently rapidly. The measured values of μ and $\mu\chi$ are therefore considered as some effective indexes of refraction and absorption [3]. The complex dielectric permeability also must be considered as the effective quantity

$$\tilde{\epsilon}_{eff} = [\mu_{eff} - i(\mu\chi)_{eff}]^2 . \quad (1)$$

Dingle [4-6] developed a theory of the anomalous skin effect and obtained a dispersion formula for the optical constants of metals in the infrared region of the spectrum. At the same time the phenomenon that reflections of the electrons from the surface of the metals takes place as specular as well as diffuse reflection was considered. The coefficient of specularity p which was introduced showed what fraction of the electrons were specularly reflected. The case $p=1$ corresponds to specular reflection, the case $p=0$ to diffuse reflections. In reality there is an intermediate value of the coefficient of specularity. Of course, the coefficient of specularity depends strongly on the quality of the surface of the metal and increases with its improvement and with a decrease in temperature.

The dispersion formula for the optical constants of metals in the infrared region of the spectrum which was obtained by Dingle [6], has after several transformations the form

$$\epsilon = \mu^2 - (\mu\chi)^2 = -\frac{\lambda^2}{c^2}\frac{\sigma}{\pi\tau} \quad (2)$$

and

$$\mu\cdot\mu\chi = \alpha\frac{\lambda^3}{c^3}\frac{\sigma}{4\pi^2\tau}, \quad (3)$$

to first order accuracy, where λ is the wave length, c is the speed of light in vacuum and

$$\alpha = 1 + \frac{3}{4}(1 - p)\frac{l}{c}\sqrt{\frac{\pi\sigma}{\tau}} . \quad (4)$$

The expression for ϵ agrees with the analogous dependence given by the classical theory of free electrons of Drude for the case

$$|\epsilon| = |\mu^2 - (\mu\chi)^2| \gg 1,$$

which for most metals is practically always true in the infrared region of the spectrum. Such an agreement, actually, was expected. The real part of the complex dielectric permeability $\epsilon = \mu^2 - (\mu\chi)^2$ was, by Drude's theory, independent of the free path length of the electrons in metals, and dependent only on the wave length and the concentration of conduction electrons. In other words the formula shows a relatively invariant character of the skin effect. The concentration of free electrons

$$N = \frac{|\epsilon|\, m^*\pi c^2}{e^2\lambda^2} = \frac{|\mu^2 - (\mu\chi)^2|\, m^*\pi c^2}{e^2\lambda^2} \quad (5)$$

found from the experimental values of the optical constants μ and $\mu\chi$ may therefore be considered as one of the basic problems of the optics of metals since the formula, in the classical sense, clearly does not depend, in essence, on the use of the model presented in reference [3].

With regard to expression (3), it agrees with Drude's expression, when the factor α is excluded. Exact agreement with Drude's theory occurs when $p=1$ and $\alpha = 1$. A good relationship between the experimental results and Drude's theory may be obtained for the anomalous skin effect, but the parameters σ and τ found at the same time do not have the same physical meaning as is used in his theory. Therefore, for the case of the anomalous skin effect, it is necessary to use Dingle's theory.

Dingle's dispersion formula may be reduced, to second order accuracy, to the form

$$\frac{(\mu\chi)^2 - \mu^2}{\lambda^2} = A - B\lambda^2 \quad (6)$$

and

$$\frac{\mu\cdot\mu\chi}{\lambda^3} = C - D\lambda^2, \tag{7}$$

where

$$A = \frac{\sigma}{\pi c^2 \tau} \tag{8}$$

and

$$C = \frac{1}{c^3}\frac{\sigma}{4\pi^2\tau^2}\left\{1 + \frac{3}{4}(1-p)\frac{1}{c}\sqrt{\frac{\pi\sigma}{\tau}}\right\}. \tag{9}$$

An expression for B and D is also given by Dingle [6]; however, a simple calculation shows that for good metals $B\lambda^2 \ll A$ and $D\lambda^2 \ll C$.

The dependences of the quantity $\frac{(\mu\chi)^2 - \mu^2}{\lambda^2}$ and $\frac{\mu\cdot\mu\chi}{\lambda^3}$ on λ^2 can be shown by straight lines on which the initial ordinates give the values of A and C respectively.

From the quantity A, determined in such a manner, and using the expression for the static conductivity

$$\sigma = \frac{Ne^2\tau}{m^*}, \tag{10}$$

one may calculate the electron concentration in the conduction band, if the effective mass m* of the electrons is known.

$$N = \frac{\pi c^2 m^* A}{e^2} \tag{11}$$

Knowing the static conductivity σ and also finding the quantity A allows one to determine the relaxation time τ

$$\tau = \frac{\sigma}{\pi c^2 A}. \tag{12}$$

According to the initial ordinate C which was found from the straight line dependence of $\frac{\mu\cdot\mu\chi}{\lambda^3}$ on λ^2 we find

$$(1-p)\,l = \frac{4}{3\pi\sqrt{A}}\left\{\frac{4\sigma C}{cA^2} - 1\right\}. \tag{13}$$

Dividing Eq (13) by Eq (12) we obtain the quantity $(1-p)v$, where $v = \frac{l}{\tau}$ is the Fermi speed of electrons. From optical measurements the separate determination of p and v is impossible.

THE DETERMINATION OF N, τ, $(1-p)l$ AND $(1-p)v$

The dependences $\frac{(\mu\chi)^2 - \mu^2}{\lambda^2} = f(\lambda^2)$ and $\frac{\mu\cdot\mu\chi}{\lambda^3} = \varphi(\lambda^2)$ constructed from previous measurements [2] of the values of the indexes of refraction μ and absorption $\mu\chi$ in the 1-12 μ region, are given in figures 1-3 for copper, gold and nickel respectively. The open circles correspond to the values $f(\lambda^2)$ and $\varphi(\lambda^2)$, constructed from experimental measurements of the quantities μ and $\mu\chi$. The dark circles correspond to the values of $f(\lambda^2)$ and $\varphi(\lambda^2)$, obtained from the smoothed curve of the dependence of μ and $\mu\chi$ on wavelength. In the latter case μ and $\mu\chi$ are taken for integer values of the wavelength.

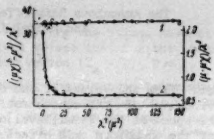

Figure 1. Copper

$1 - f(\lambda^2)$; $2 - \varphi(\lambda^2)$.

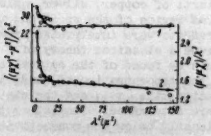

Figure 2. Gold

$1 - f(\lambda^2)$; $2 - \varphi(\lambda^2)$.

The upper curve presents the dependence of $f(\lambda^2)$; and corresponding ordinate scale is marked at the left. The lower curve gives the dependence of $\varphi(\lambda^2)$; it ordinate scale is marked on the right.

Extrapolating the linear portion of the $f(\lambda^2)$ and $\varphi(\lambda^2)$ curves to the intersection with the ordinate axis at the point $\lambda^2 = 0$ gives the corresponding values of the constants A and C. Equation (11) allows the concentration of conduction electrons N to be calculated. As is expected, the concentration of free electrons determined from the constant A agrees with the value obtained earlier [2] on the basis of Drude's classical theory of free electrons. If it is assumed that the conductivity σ of our samples is equal to the conductivity of the bulk metal [7], then by equation (12) it is possible to calculate the relaxation time τ. Equation (13) gives the value of the quantity $(1-p)l$, if the known value of σ and the experimental values of A and C are used.

Copper (Fig. 1). The linear dependence of $f(\lambda^2)$ is well satisfied over the entire investigated region. The quantity $f(\lambda^2)$ remains constant over all wavelengths. The dependence $\varphi(\lambda^2)$ retains a linear character only for wave lengths larger than 5μ.

Silver. The quantity $f(\lambda^2)$ increases with increasing wave length λ. The measurment of the optical constants of silver are connected with large experimental difficulties, therefore μ and $\mu\chi$ are determined less exactly than for other metals and this may be one of the reasons for such a dependence of $f(\lambda^2)$. On the other hand, a very good linear dependence of $\varphi(\lambda^2)$ which decreases with increasing wavelength from 1.04 (at λ = 1μ) to 0.98 (at 12μ) is observed for silver. The quantity A was calculated for silver from equation (11) using the value of N, found earlier [1,2] on the basis of Drude's classical theory of free electrons, and the quantity C by the method described above.

Gold (Fig. 2). The quantity $f(\lambda^2)$ was constant for wavelengths larger than 4μ, and equal to $25\times10^{8}\,cm^{-2}$. The dependence of $\varphi(\lambda^2)$ also has a linear character for wave lengths larger than 4μ, while at the same time $\varphi(\lambda^2)$ decreases more strongly with increasing wave length than either copper or silver.

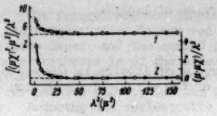

Figure 3 Nickel
1 - $f(\lambda^2)$; 2 - $\varphi(\lambda^2)$

METAL	$A \cdot 10^{-8}$ (cm-2)	$C \cdot 10^{-12}$ (cm^{-3})	$\sigma \cdot 10^{-16}$ (CgE) [7]	$N \cdot 10^{-22}$ (cm^{-3})	$\tau \cdot 10^{14}$ (sec)	$(1-p)l \cdot 10^{5}$ (cm)	$(1-p) \cdot v \cdot 10^{-8}$ (cm/sec)
Copper	34.1	0.65	58	3.8 *	6.05	2.43	4.02
Silver	64.2	1.05	61	7.2	3.36	0.57	1.7
Gold	25	1.58	44	2.8	6.23	11.7	18.8
Nickel	4.15	0.3	13.7	0.46**	11.7	64.1	55

*If, in agreement with [8], it is assumed that $m^* = 1.47m$, then $N = 5.57 \times 10^{22}$ cm^{-3}

**If, in agreement with [8], it is assumed that $m^* = 2m$, then $N = 12.95 \times 10^{22}$ cm^{-3}

Nickel (Fig.3). The quantity $f(\lambda^2)$ is linear and constant only in the region of wave length larger than 8μ. The quantity $\varphi(\lambda^2)$ changes linearly with λ^2 in the same region as $f(\lambda^2)$, insignificantly decreasing with increasing wave length.

In the table the values of A and C found by the methods described above and the calculated values of N, τ, (1-p)l and (1-p)v are given.

The values of the conductivity of these metals given in the table are from reference [7].

In conclusion the authors express sincere thanks to K. D. Sinel'nikov for consideration and great interest in the work.

November 26, 1958

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New Interferometric Method of Measuring the Dispersion of Liquids

I. N. SHKLIAREVSKII

Abstract: A new interferometric method of measuring the dispersion of liquids in the visible and ultraviolet regions of the spectrum is described. The method is free of the effect of dispersion of phase change and permits increased precision of measurement.

We have earlier developed an interferometric method of measuring the dispersion of liquid and solid substances (films) in the visible [1] and ultraviolet [2] regions of the spectrum. We have pointed out [1-3] that with its express advantages by comparison with the method of I.V. Obreimov [4] (high luminosity), our method had an essential shortcoming--lower accuracy. In spite of the fact that the wavelengths of lines of even order may be measured with very high precision, diregarding the dispersion of phase change arising at the dielectric-metal boundary would not afford the possibility of obtaining the required accuracy. This shortcoming in the proposed method is here removed. The influence of the dispersion of the phase change is excluded in exactly the same way as in the method of measuring the thickness of thin films [5].

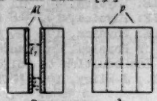

Figure 1

One of the interferometer plates is ground to form a step of 2-3μ thick. The second plate is flat. The inner surfaces of the plates are partially covered with a semi-transparent film of silver or aluminum (for measurements in the ultraviolet). The cross-section of the plate is shown in figure 1,a. Grooves are cut by a ruling engine through the metal film on the stepped plate in several places as shown in figure 1,b. These grooves P later play the part of reference marks.

Connected together, the plates are placed before the slit of spectrograph as in figure 2. Two systems of lines of even order appear in the focal plane of the camera objective, corresponding to the two different air gap thicknesses.

With the help of a mounting on which the plates are fastened, they may be displaced in a horizontal direction parallel to the plane of the spectrograph slit, so that the slit cuts out successively narrow parts of the gap. If a groove is imaged on the slit, the interference pattern will disappear. This position is recorded on the drum of the micrometer screw of the mount. The positions of two or three groove reference marks are noted in this way. Thereafter comparative reference marks are selected in several parts of the plate for which exact measurements of step thickness have been made.

Inasmuch as the thickness of a step is a small number of microns, a vernier effect occurs. The wavelength λ of any coincident lines belonging to two systems is measured. The orders of interference m and n are determined, and by the formula

$$t = \frac{m - n}{2}\lambda \qquad (1)$$

the thickness t of the steps is found (see [5]). Since the wavelength of coincident lines may be determined with a precision of a tenth of an Angstrom, the size of the step in a given fixed place is established with a similar high accuracy.

Figure 2

Q--light source K--condenser S--diaphragm with pinhole aperture L_1 and L_2--objectives p--coupled plates S_p--spectrograph slit

Having filled the gap between the interference plates with the liquid to be investigated and having chosen one of the steps at a place for which the thickness has been measured, the interference pattern is photographed. Here, in contrast to [1,2], it is more advantageous to work with interference fringes of low order.

For each system of fringes it is possible to write accordingly the following set of equations

$$\begin{cases} 2t_1\mu_1 - \dfrac{\delta_1\lambda_1}{\pi} = (m + i)\lambda_1, \ (i = \pm 0,1,2,\ldots), \\ 2t_2\mu_i - \dfrac{\delta_1\lambda_2}{\pi} = (n + i)\lambda_1, \ (i = \pm 0, 1,2,\ldots), \end{cases} \qquad (2)$$

where t_1 and t_2 are the air gap thicknesses.

As is evident from equation (2), the position of the interference fringes of the spectrum is determined by the optical thickness of the gap and the phase change arising from the reflection of light at the transparent dielectric-metal boundary. In this connection we point out the incorrect assertion of Kostyshin [6], that in the case of a transparent layer bounded by the same arbitrary medium, the location of the minimum will not depend on the magnitude of the phase change. The incorrectness of this follows even from the presence of the dispersion of phase change. Further, if half of a very thin sheet of mica is covered on both sides with a uniform coating of silver and the other half with aluminum coatings, displacement of the interference bands may be observed associated with different phase changes at the mica-silver and mica-aluminum boundaries. The application of a uniform metal coating despite [6] presents no difficulties.

The second statement in the paper [6], that the location of the interference bands in the general case depends on the reflectivity of the boundary, cannot be regarded as correct. Fizeau fringes, observed with light normally incident on a wedge-shaped layer of ZnS deposited on glass or metal, are not displaced when part of the layer is wet by any transparent liquid. The reflectivity of the ZnS-liquid boundary may hence be changed by several times compared with the reflectivity of the ZnS-air

boundary. The fringes are not displaced where part of the wedge surface is covered by an opaque silver layer, and the second part by a layer whose thickness is of the order of 5×10^{-6} cm. The optical constants of such a layer are the same as for massive silver, but the reflectivity is lower. Reducing the reflectivity results only in making the bands diffuse.

The conditions for the extrema of layers deposited on absorbing substrates, and the introduction of phase changes in the formula for the intensity of light, are incorrect in the paper [6]. The last case arises from the previously mentioned oversight. In noting this oversight in the paper [6], we do not wish to disparage the results of the measurements inasmuch as the influence of the factors the author examined are completely negligible.

If the functions $\frac{m\lambda}{2t} = f(\lambda)$ and $\frac{n\lambda}{2t} = \varphi(\lambda)$, where $t = t_1 - t_2$ is the step thickness, are plotted on a large sheet of millimeter paper, the difference of the ordinates of these two curves at any wavelength gives the magnitude of μ. Here the dispersion of the phase change is excluded.

The order of interference may be established as follows. Let λ_0 and λ_1 be the wavelengths of neighboring lines. If the refractive indices of the liquid under study at these wavelengths, μ_0 and μ_1, are not greatly different from each other, then

$$m = \frac{\lambda_1}{\lambda_0 - \lambda_1}, \tag{3}$$

in which m must be rounded off to a whole number. For the determination of the true value of the interference order, the m found in this way must be diminished by unity (see [3]). The interference orders of the rest of the lines are found in the usual way.

Equation (3) results from the more exact expression

$$m' = \frac{\lambda_1/\mu_1}{\lambda_0/\mu_0 - \lambda_1/\mu_1} \tag{4}$$

if in the latter it is assumed that $\mu_0 = \mu_1$. Hence $m < m'$. If the dispersion of the liquid under study is low, the decrease in m is not as great, so that the rounding off of the computed value of m to a whole number will be in error by unity. Still, such an error is not excluded in the case of liquids of high dispersion. This error can be eliminated.

In the case of an air gap the curve $f(\lambda)$ is inclined toward the long wavelength side. This is explained by the fact that $\frac{\delta_1 \lambda_1}{\pi}$ in the equation

$$2t - \frac{\delta_1 \lambda_1}{\pi} = (m+i)\lambda_1, \quad (i = \pm 0, 1, 2, \ldots) \tag{5}$$

decreases with decreasing wavelength. The slope of the curve $f(\lambda)$ is determined by the dispersion of the phase changes and does not depend on the gap width (magnitude of the interference order).

If the space between the plates is filled with a liquid, the slope of the corresponding curve is determined not only by the magnitude of the dispersion of the phase change, but also by the dispersion of the liquid. Moreover, the slope specified by the dispersion of the liquid depends on the thickness of the gap.

For the extreme lines of even order λ_0 and λ_k of a particular spectral region equations similar to (2) may be written. Subtracting term by term we obtain the quantity

$$\frac{1}{2}[(m+k)\lambda_k - m\lambda_0] = t_1(\mu_k - \mu_0) + \left(\frac{\delta_0 \lambda_0}{\pi} - \frac{\delta_k \lambda_k}{\pi}\right), \tag{6}$$

which determines the slope of the curve $f(\lambda)$ in the given spectral region. A numerical value for the right side of Equation (6) may be estimated approximately. If it agrees with that of the left side, the orders are correctly determined.

We shall consider the following example. Let $\lambda_0 = 6458.7$ Å and $\lambda_4 = 5247.1$ Å. Let the space between the interferometer plates be filled with commercial glycerine. The orders of the wavelengths determined from (3) are 17 and 21, but the actual orders are respectively 16 and 20. The refractive indices μ_0 and μ_4 of glycerine are approximately 1.47 and 1.475 (preliminarily measured on a refractometer). The refractive indices of silver $(\mu\chi)_0$ and $(\mu\chi)_4$ are equal to 4.2 and 3.2. Using the approximate equality

$$\tan\delta = \frac{2\mu_d \mu\chi}{\mu_d^2 - (\mu\chi)^2}, \tag{7}$$

where μ_d is the index of refraction of the dielectric, it is possible to determine δ_0 and δ_4, then the second term of the right hand side of Equation (6) can be computed. The order is found to be 600: The spacing width is $t = \frac{m\lambda_0}{2\mu_0} = 3.73$ microns. Even in the case where m is incorrectly determined, the order of the gap thickness is not altered. Since $\mu_4 - \mu_0 = 0.005$, the first term on the right side of (6) will be equal to 186. The sum of the two terms on the right side of (6) are of the order 800. We shall now evaluate the differences $\frac{(m+4)}{2}\lambda_4 - \frac{m\lambda_0}{2}$, giving m the values 18, 17, 16, 15. They become equal to 410, 196, 802, and 1408. The third difference agrees well, but the others differ widely from the computed magnitude. This serves as a criterion for the choice of order.

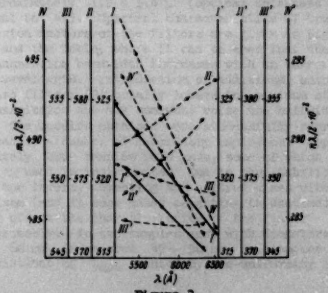

Figure 3

In Figure 3 the curves $f(\lambda)$ and $\varphi(\lambda)$ are drawn. The end points of the principal curves were taken from the preceding example. The curves I, I' correspond to correctly chosen orders; curves II, II', III, III' are higher correspondingly by two orders and one order; the curves IV, IV' are lowered by one order. The slope of the curves $\varphi(\lambda)$ corresponding to the lowest orders because of the smaller space between the interferometer plates, is smaller than the slope of the curves $f(\lambda)$.

Such verification is necessary for investigation of liquids which possess large dispersion. For the same step size the difference between curves similar to those given in Figure 3 will be the larger, the greater the dispersion of the liquid.

Our proposed interferometric method of measuring the dispersion of liquids is equally useful in the ultraviolet region of the spectrum. In this case an iron arc or spark might serve as the radiation source. The method of measurement for this case is described in [2].

The participation of G. N. Poliakov and E. T. Verkhovtsev in the experimental testing of the new method of measurement of the dispersion of liquids is acknowledged.

In conclusion, the author wishes to use this occasion to express his profound gratitude to K. D. Sinel'nikov for his consideration and interest in this work.

December 20, 1958

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Interference Light Filters of Multilayer Dielectrics

T. N. KRYLOVA

Abstract: Characteristics are given of interference light filters, consisting of alternate layers of dielectrics (titanium dioxide and silicon dioxide), obtained from easily hydrolyzing compounds. By replacing the transparent layers of silver with multilayer dielectrics, filters were obtained which passed 80% of the light with negligible bandwidths. Using the indicated substances samples of stable filters for the range 380 - 850 mμ were obtained.

1. DESCRIPTION OF THE PROBLEM

At the present time in order to obtain monochromatic light interference, light filters are widely used which have a high transmission factor at negligible bandwidth. The theory and practice of obtaining interference filters has been described in the literature [1]. Among the numerous types the light filter of Fabry and Perot has been most widely used. This filter consists of a glass plate of several square centimeters in area, with two layers of transparent silver, with a high reflection coefficient deposited on its surface and separated by a dielectric layer of low refractive index. The optical thickness of the latter determines the location of the spectral range of transmission of the light filter.

Theoretical calculations [2,3] show that an interference light filter with layers of silver used in the visible region of the spectrum passes 45-50% of the light at half-bandwidth, which is of the order $\frac{\lambda}{80}$ (5 - 10 mμ). The values obtained experimentally are usually lower.

The first interference filters were obtained by Geffken [2]. At the present time they are made in many countries [4].

Due to partial absorption of the light by the layers of silver the light filters described above do not have a high transmission factor. Their other shortcoming is the tendency of silver to oxidize, which in time leads to a displacement of the band and a reduction in the maximum transmission. As the papers of the last few years have shown, [5], replacing the silver with multilayer dielectric coatings with high coefficients of reflection (and no absorption) makes it possible to obtain light filters which pass 80 to 90% of the light at the same small half-width. Individual samples of such filters were obtained by Dufour [6], Polster [7] and others by depositing films of zinc sulfide and cryolite in vacuum and have shown good results.

2. EXPERIMENTAL DATA.

It was shown by the author of this article [8], that depositing multilayer coatings of alternate layers of titanium dioxide and silicon dioxide, obtained from alcohol solutions of easily hydrolizing ethyl ethers of orthotitanic and orthosilicic acids with subsequent thermal processing, increases reflection from the surface of the glass from 4 to 90% and higher in different regions of the spectrum from 380 to 1200 mμ. The layers are stable and mechanically strong. The use of these coatings made it possible to obtain interference light filters with narrow transmission bands for a wide range of the spectrum.

The diagram of a light filter consisting of 15 layers is given in Figure 1. Tha making of such a light filter consists of depositing a 7-ply coating of alternate layers of titanium dioxide and silicon dioxide, each $\frac{\lambda}{4}$ thick, on the surface of a glass plate, then a layer of silicon dioxide $\frac{\lambda}{2}$ thick, and another 7-ply coating similar to the first one. The optical thickness of the layers determines the region of the narrow transmission band.

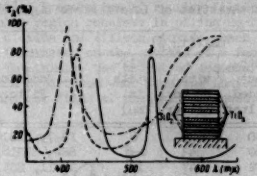

Figure 1. Spectral curves of the transmission factor of filters with different numbers of layers. On the right - diagram of a light filter with 15 layers. Other information is in the text.

Experimental samples using 3-, 5-, and 7-ply coatings were prepared, reflecting 50, 80, and 90% of the light respectively. In Figure 1 results are given of measuring transmission factors of light filters with 7 (curve 1), 11 (curve 2), and 15 (curve 3) layers. The 15-layer light filter passes up to 80% of the light in the 530 mμ range at a halfwidth of 10 mμ, but further on the transmission factor rises rapidly. The spurious maxima must be removed by means of additional filters which usually consist of colored glasses of appropriate types.

Filters with narrow transmission bands for the range 380 - 600 mμ were obtained using 7-ply coatings and had characteristics close to curve 3 (Fig. 1). The total thickness of the layers was approximately 1.2 - 1.4 μ (optical thickness equal to 4λ). Spectral characteristics of transmission factors of the filters are given in Figure 2 and the Table, where it can be seen that the transmission bandwidth increases with an increase in wavelength. Introduction of additional colored glass filters [9] usually lowers the maximum of transmission and may somewhat raise the halfwidth.

The results obtained were successfully reproduced by a number of laboratory employees: approximately 200 samples were made, some of which are being used in instruments. Due to the stability of the layers, cementing the colored glass with balsam (and in some cases cementing in acetone) did not affect the characteristics of the filter noticeably. In the samples made with diameters up to 60 mm, in an area 45 - 50 mm in diameter deviations of λ_{max} caused by non-uniformity of

the coating, were approximately ±1mμ.

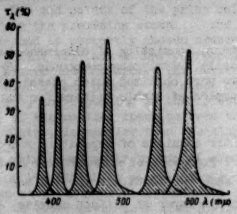

Figure 2. Spectral characteristics of complete light filters.

Characteristics of Interference Light Filters

λ_{max} (in mμ)	τ_{max}.(in %) without added filter	τ_{max}.(in %) with added filter	Half-width (in mμ)	Additional Filters
386	50	35	6	FS-7, SZS18
405	60	43	8-6	SS4, SZS18
440	72	47	10	ZHS11, SS5, SZS18
477	70	54	10	ZHS12, SZS18
549	60	45	11	OS11, SZS18
589	70	50	12	SZ14, SZS10

A further increase in the number of layers of the multilayer coating improves the characteristics of the filters, although difficulties of technological nature such as cracking and peeling of thick films limits this increase. For the same reason filters for the wavelength range of 700 mμ and higher were made with fewer layers.

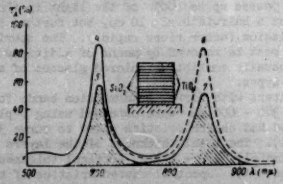

Figure 3. Spectral curves of the transmission factor of filters for long wavelengths.

The possibility was investigated of making a light filter with an intermediate higher refractive index dielectric layer between the two 6-ply coatings. The diagram and a typical curve of the transmission of such a filter (curve 4) is shown in Figure 3. The filter passes more than 80% at 700 mμ at a halfwidth of 28 mμ; the background is 8-10%. As additional filters for removing secondary maxima and reducing the background, a KS17 red glass and a multilayer interference light divider [8] with high reflection coefficients in the 800-900 mμ range were used (for lack of colored glass of proper characteristics). The complete light filter (Fig. 3, curve 5) transmits 56% at a halfwidth of 23 mμ and has a background of a few tenths of a percent which begins to rise at 1000 mμ. Filters for long wave-lengths were obtained also by using alternate 5-ply coatings with a separating layer of SiO_2. To reduce the background two identical light filters were used as a pair. The spectral curve of the double filter is given in Figure 3 (curve 6). The filter transmits in the range of 850 mμ more than 80% of the light at a halfwidth of the order of 35 mμ and a background of 2-5%. In combination with FS7 and KS15 colored glass [9] the maximum of transmission decreases to 50% and the halfwidth assumes a value close to 30 mμ; the background disappears completely (Fig. 3, curve 7).

June 11, 1958.

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Interference Filters for the Ultraviolet Region of the Spectrum

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Abstract: Multilayer coatings of alternate layers of thorium dioxide and silicon dioxide, transparent in the 220-400 mμ band, are described. These coatings, which selectively increase the reflectance of a quartz surface to 95%, may be used as reflecting filters. Stable interference filters can be prepared for the 250-400 mμ band, with peak transmittances ≤ 80% and half-widths of 6-14 mμ.

INTRODUCTION

For some time past, there has been widespread application of multilayer interference coatings of dielectrics permitting a decided decrease or increase in the intensity of light reflected from the surface of an optical medium. These coatings have also been used to bring about a spectral partition of light into reflected and transmitted components, to isolate a narrow band of the spectrum, etc. Interference filters of various constructions are described in [1]. There are a number of possibilities for preparation of interference filters in the visible region but the situation is not nearly as favorable in the ultraviolet. This is explained by the lack of film-producing materials giving stable coatings which are transparent in the short wavelengths, especially in the 200-300 mμ region.

During the past 2-3 years, several investigations were conducted along the lines with the aim of increasing the resolving power of the Fabry-Perot interferometer in the $\lambda \leq 3000$Å region. The commonly used transparent layers of aluminum possess appreciable absorption in the $\lambda < 3000$Å region. Here, as well as in the visible band of the spectrum, metallic layers were replaced by multilayer dielectric coatings.

Thus, in the 3000-4000 Å, Penselin and Steudel [2] used films of lead chloride and magnesium fluoride as well as antimony trioxide and cryolite. Nine alternate layers increase the reflectance of quartz up to 96%, with an absorption of ~1.9%.

For the 2500-2600Å region, Rimbert, Lennuier and Cojan [3] recommend a ten-layer coating of rubidium iodide and cryolite. Steudel and Stotz [4] found that eleven-layer coatings made up with cesium iodide (transparent in the 2500-3000Å region) or cesium bromide (transparent in the 2300-2500Å region) alternating with cryolite or magnesium fluoride, reflect up to 95% and absorb ~< 5% in the region indicated. However, according to the authors themselves, all of the abovedescribed coatings are unstable and deteriorate easily due to atmospheric moisture. Even after when covered with protective coatings, they last only a few days. Films of antimony trioxide prove to be an exception, not requiring protection. With the aid of these films, Barr and Jenkins [5] obtained an interference filter with a narrow transmission band (~ 100Å) for λ = 3725Å.

Interference filters for the 220-400 mμ band using layers of silver and certain other metals are also described in [6, 7].

A chemical method of obtaining surface films from easily hydrolyzed solutions gives mechanically strong and chemically stable layers of thorium dioxide and silicon dioxide, transparent in the 220-400 mμ region [8, 9]. With the help of layers of thorium dioxide (index of refraction 2.0) and silicon dioxide, (refractive index 1.45), we obtained many multilayer reflecting filters and interference filters with narrow transmission bands for operation in the indicated region of the spectrum.

MULTILAYER REFLECTING FILTERS

Chemical methods for producing multilayer filters for the visible region, as well as their spectral characteristics, were described in our earlier paper [10]. Preparation of similar filters for the ultraviolet region consists in piling up layers of thorium dioxide and silicon dioxide, each of $\lambda/4$ optical thickness, on the surface of a fused quartz plate. To minimize the height of secondary maxima, one should depart somewhat from the indicated values and use films of unequal thickness.

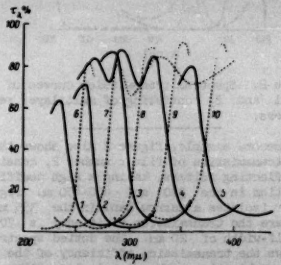

Figure 1. Curves showing transmission efficiency τ_λ of multilayer reflection filters (1-10), as a function of wavelength.

Technical difficulties were encountered in attempting to prepare highly reflecting filters in the 300-400 mμ region. Multilayer films thicker than 1 μ became crazed and fell off. In order to circumvent this difficulty, it became necessary to use solutions of low concentration and to build up each $\lambda/4$ layer out of two or three layers.

A reflecting filter consisting of 11-15 alternating layers of thorium dioxide and silicon dioxide reflects 90-95% of the incident light at the peak, the position of which is determined by the optical thickness of the layers. The spectral characteristics of several reflecting filters are shown in figure 1, which gives spectral transmission values, measured by means of a photoelectric spectrophotometer. From figure 1, it is seen that the width of a high reflection band, where transmission does not exceed 5%, is $\lambda/6 - \lambda/8$; on either side of this band, the curve rises sharply and the transmission efficiency

approaches 90-80%. Such reflecting filters may find diverse applications. They may be used for the isolation of various portions of the spectrum.

By arranging a collection of these devices, it is possible to construct filters possessing various characteristics. On Figure 2, for example, the solid curve shows the transmission of filter number 1, composed of four reflecting filters; two reflect 95% in the 320-360 mμ region; two behave similarly in the 360-400 mμ region. The composite system transmits 50-60% of the radiation in the 250-300 mμ region, but no more than 0.2 - 0.5% in the 320-400 mμ region. In order to dispose of the side-bands in the 400 mμ region, one may use an auxiliary colored glass filter (UFS-1). The overall spectral characteristic of this filter is given by dashed curve 1a in figure 2.

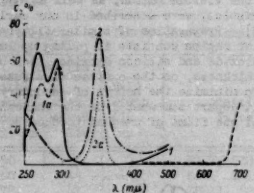

Figure 2. Spectral transmission curves of filters 1 and 2, consisting of multilayer reflection filters.

As a second example, figure 2 also shows the spectral transmission of filter number 2, consisting of two reflecting filters, having a high coefficient of reflection in the 320 and 400-450 mμ regions. The filter isolates a narrow band in the 355 mμ region where the transmission efficiency is 70% with a half-width of 20 mμ. The dotted spectral curve shows the transmission efficiency of the same filter in combination with colored glass filters UFS-2 and BS-6.

INTERFERENCE FILTERS

A further extension of the project consisted in the creation of filters with a narrow transmission band, similar to interference filters. These filters utilized transparent layers of silver and were fairly transparent in the ultraviolet region. The visible range filters which we prepared [11] by a chemical solution process showed both good optical characteristics and acceptable mechanical and chemical rigidity and stability.

The ultraviolet interference filters which we constructed were of two types. In filters of type I, an intermediate $\lambda/2$ layer of silicon dioxide was placed between two seven-layer coatings of alternating layers of thorium dioxide and silicon dioxide. In filters of type II, the intermediate $\lambda/2$ layer consisted of thorium dioxide, and was placed between two six-layer coatings. In the second case it was possible to have a filter with fewer layers, which was technologically more advantageous.

Figure 3 shows spectral curves of transmission efficiency for three filters. Filter 2, (type I) transmits 72% in the λ=280 mμ region, with a half-width pass band of 6 mμ. Filter 3 (type II) has a pass band of 12 mμ half-width at 370 mμ, where it transmits ~80%; the background amounts to from 6 to 10% in both cases. In the figure, curves 2a and 3a, indicate the transmission efficiency of these filters in combination with the colored glass filters which eliminate side-bands. Unfortunately, colored glass filters cannot remove the background in the 300-400 mμ region; in this case, we had to resort to the multilayer reflecting filters described in the preceding portion of this paper. This filter thus operates in combination with a glass UFS-1 filter and four reflecting filters. This filter transmits 30%, with a half-width band of 8 mμ (see curve 2a). In filter 3, glasses NS-1 and SZS-10 were used. The completed filter transmits 57% with a half-width of 12 mμ (Fig. 3, curve 3a).

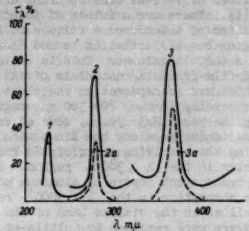

Figure 3. Spectral characteristics of interference filters for the ultraviolet region.

It was impossible to find glass filters to supplement the 230-250 mμ interference filters by absorbing side-bands. Figure 3 shows the characteristic of filter 1, passing 37% of the radiation in the 230 mμ region, with a half-width of 8 mμ (curve 1).

Characteristics of Interference Filters for the Ultraviolet Spectral Region.

	Without Auxiliary Filters		With Auxiliary Filters			
Location of transmission max. (in mμ)	Transmission at peak (in %)	Half-width (in mμ)	Transmission at peak (in %)	Half-width (in mμ)	Auxiliary Filters	Background absent in regions (in mμ)
250	53	8	–	–	—	—
270	65	6	27	8	UFS-1 & reflection filter	200-690
290	76	6-8	33	8	UFS-1 & reflection filter	200-690
310	76	12	38	6	UFS-2, interference filter, reflection filt.	200-690
330	83	14	43	10	UFS-1, SS-6, reflection filt.	200-690
390	82	14	40	16	UFS-1, SZS-18	200-1000

The table lists the characteristics of several filters possessing pass bands in the 230-400 mμ range. Type I filters operate in the 230-300 mμ range; type II filters operate in the 300-400 mμ range. With the aid of colored glass and interference reflection filters, it is possible to suppress the background in the whole visible region up to 690 mμ, and in certain cases even to 1μ.

Filters of alternating layers of thorium dioxide and silicon dioxide are sufficiently stable and do not require special protection from the atmosphere.

July 10, 1958

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On the Choice of Scanning Rate, Optimum Time Constant and Slit Widths for Spectrometer Measurements

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Abstract: The optimum conditions for recording spectra have been derived from the conditions for minimum total mean square error. By considering the case of small systematic errors, results have been obtained which are applicable to a wide range of sets of observational data, apparatus functions and characteristics of recording systems.

The choice of optimum conditions for the recording of spectra has been discussed repeatedly. In references [1, 2] the requirement of minimum total mean-square error was used to derive the optimum values of slit-width and degree of absorption for the case in which the distortion introduced into the scanning as a result of the inertia of the recording system is negligible and the time constant is fixed.

In other references, [3-8], however, and in a review article, [9], the question of the influence of the inertia of the recording system on the observed spectra was considered more carefully. Recommendations on the choice of measuring conditions are given in references [4, 7, 8, 9]. In contrast to [1, 2], these recommendations were derived not from the condition of minimum total error but rather from the requirement that a previously given signal-to-noise ratio and scanning error be achieved. In reference [6], the measuring conditions recommended were derived from a requirement on the minimum systematic error for a given signal-to-noise ratio.

As will be shown below, the measuring conditions derived as above do not in general correspond to the optimum conditions from the point of view of obtaining the smallest total error.

One may approach the choice of the optimal conditions, taking account of the inertia of the recording system, in the fashion of references [1,2], i.e. one may pose the following problem: For what parameters of a given system, controllable by the investigator, may one obtain the smallest total error in the measurement of an arbitrary spectral characteristic of a given substance (for example the line intensity at the maximum or the line-width). One may also pose the reverse problem: For what characteristics of the system and for which measuring conditions may one obtain a given accuracy in a given time of measurement.

In the present article the above problems are solved under an assumption which is not equivalent to the assumption of an idealized apparatus.

We first consider systematic distortions and errors. Let the distribution $\varphi(\lambda)$ be measured by a spectral apparatus having an apparatus function $a(\lambda)$. As is well known, the distribution at the exit of the apparatus $f(\lambda)$ may be described in this case by the product of the functions $\varphi(\lambda)$ and $a(\lambda)$. With the help of the Fourier transform one can then write

$$F(\omega) = \Phi(\omega)\, A(\omega)$$

and

$$(1) \qquad f(\lambda) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \Phi(\omega)\, A(\omega)\, \exp[i\omega\lambda]\, d\omega$$

where $\Phi(\omega)$, $A(\omega)$ and $F(\omega)$ are the Fourier transforms of $\varphi(\lambda)$, $a(\lambda)$, and $f(\lambda)$. Furthermore if the distribution is scanned at a constant rate $v = \frac{d\lambda}{dt}$ and recorded with the help of a recording system possessing inertia, then for the distribution $h(\lambda) = h(vt)$ obtained at the exit of the system one may write by analogy with (1)

$$(2) \qquad H(\omega) = F(\omega)K(\omega) = \Phi(\omega)A(\omega)K(\omega);$$

$$h(\lambda) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \Phi(\omega)A(\omega)K(\omega)\exp[i\omega\lambda]\, d\omega$$

where $H(\omega)$ is the Fourier transform of $h(\lambda)$, and $K(\omega)$ describes the inertial properties of the recording system [$K(v\omega) = K(2\pi\nu)$ is simply the complex frequency characteristic of the system].

The form of $h(\lambda)$ and hence the systematic errors depend on the form of $\varphi(\lambda)$, $a(\lambda)$ and $K(\omega)$. It is therefore usual in the solution of such problems to assume a definite form for these functions. This is done in detail in [1-9]. On the contrary, in the present article we will not proceed from an assumed form for φ, a, and K, but rather from the assumption that the systematic errors are small.* Under this condition it turns out to be possible to analyze the question of systematic error for the general case and to give general rules which are valid for a wide class of functions, and also to explain the influence of the form of the functions under consideration.

The condition of small systematic error means that $A(\omega)$ and $K(\omega)$ differ very little from 1 in the region ω where $\Phi(\omega)$ is significantly different from 0, [here it is assumed that the corresponding functions are normalized so that the area $\varphi(\lambda)$ remains constant in magnitude, i.e. $A(0)=1$, $K(0)=1$]. We can write $A(\omega)$ and $K(\omega)$ in the form

$$A(\omega) = |A(\omega)|\exp[-i\eta(\omega)],\quad K(\omega) = |K(\omega)|\exp[-i\kappa(\omega)]$$

and we expand them in this region in a series in powers of ω. We recall that $|A(\omega)|$ and $|K(\omega)|$ are even functions and that the phases $\eta(\omega)$ and $\kappa(\omega)$ are odd. Moreover the effect of the apparatus function and the inertia of the recording system is usually to decrease $\Phi(\omega)$ for large ω. Hence we will assume that the functions of interest to us may be written in the first non-vanishing approximation in the form

*We note that, except in the case of a reduction to an ideal apparatus, the condition that the systematic error be small is almost always satisfied if one speaks in terms of measurements of 10-15% accuracy in intensities or 20-30% in optical density, respectively.

(3) $$A(\omega) \approx (1 - a\alpha^2\omega^2) \exp[-i\omega\eta];$$

(4) $$K(\omega) \approx (1 - b\tau^2\nu^2\omega^2)\exp[-i\omega\kappa\nu].$$

Here α and $\tau\nu$ are parameters with the dimensions of λ (τ is a parameter with the dimensions of time), determining the width of $|A(\omega)|$ and $|K(\omega)|$; a and b are numerical coefficients whose magnitudes depend on the form of $A(\omega)$ and $K(\omega)$ respectively, and η and $\kappa\nu$ are parameters determining the phase shifts. With the help of (2), (3) and (4) it is not difficult to show that (cf. for instance reference[10])

(5) $$h(\lambda)=\varphi(\lambda-\eta-\kappa\nu) + \varphi''(\lambda-\eta-\kappa\nu)(a\alpha^2 + b\tau^2\nu^2).$$

Thus under our assumptions, the effect of the apparatus function is to change the true distribution by an amount $a\alpha^2\varphi''$ and to shift it by η [if $a(\lambda)$ is symmetrical then $\eta=0$]; analogously the effect of the recording system is to give a systematic error $b\tau^2\nu^2\varphi''$ and a displacement $\kappa\nu$. As may be seen from (5), the magnitude of the displacement does not depend on λ. Hence such a displacement may easily be taken into account by a proper re-calibration, and will then introduce no further error. In the future we will assume that this has been done and will consider only errors connected with a change in the magnitude of $\varphi(\lambda)$. Hence we put

(5a) $$h(\lambda)=\varphi(\lambda)+\varphi''(\lambda)(a\alpha^2+b\tau^2\nu^2).$$

The results obtained are applicable for those $a(\lambda)$ for which (3) is satisfied; for instance, for a Gaussian apparatus function, or for an apparatus function due to an arbitrary number of slits of various widths, or for the apparatus function of a phototube. (We note that for all of these functions $\eta=0$). However the dispersion and diffraction "apparatus functions" are not included in this scheme since for them $A(\omega)=1-a\alpha|\omega|$ for $|\alpha\omega| \ll 1$. As far as the expansion (4) is concerned we will show only that it holds for an arbitrary sequence of non-interacting RC integrating circuits.

Furthermore, for simplicity, we limit ourselves henceforth to the case where $\varphi(\lambda)$ is a function of two parameters: φ_o, the intensity at the maximum, and a parameter γ which determines the line width.

In this case we may write

(6) $$\varphi''(\lambda) = r(\lambda)\frac{\varphi(\lambda)}{\gamma^2},$$

where the factor $r(\lambda)$ depends on the form of φ.

For $h(\lambda)$ we now obtain an expression giving the systematic errors

(7) $$h(\lambda)=\varphi(\lambda)\,[1 + r(\lambda)(az^2 + by^2)],$$

where we have introduced the dimensionless parameters $z = \frac{\alpha}{\gamma}$ and $y = \frac{\tau\nu}{\gamma}$.

We now apply these results to the measurement of optical density. In reference [1] a general formula was derived for the total relative mean square error in measuring the optical density D. For the case of a non-ideal apparatus and in the absence of a constant background absorption this formula has the form

(8) $$F^2 = \frac{\overline{\Delta D^2}}{D^2} = M(x)\left\{\left[1 - \frac{h(\lambda)}{\varphi(\lambda)}\right]^2 + \frac{\overline{\Delta\varphi^2}}{x^2I^2}\right\}.$$

Here $x(\lambda)= \frac{\varphi(\lambda)}{I}$ is the actual absorption, I is the difference in scale readings between total transmission and total absorption, $h(\lambda)/I$ is the absorption observed at the exit, $[1-h(\lambda)/\varphi(\lambda)]^2$ - is a term describing the systematic errors, $\frac{\overline{\Delta\varphi^2}}{x^2I^2}$ -is a term describing the random errors, and

$$M(x) = \left[\frac{x}{(1-x)\ln(1-x)}\right]^2$$ - is a factor which enters when the error in optical density is estimated from the error in absorption. Here we are not taking account of so-called "mechanical" errors in the measurements (cf.[1]), since for the case of a non-ideal apparatus they play only a small role. Now if the noise in the sensing device has a "white" spectrum, then the random error may be written in the form (cf. for example [6-9])

(9) $$\frac{\overline{\Delta\varphi^2}}{I^2} = \frac{E}{\tau S^4},$$

where S is the width of monochromator slits, which are assumed to be equal, $\frac{1}{\tau}$ is a parameter which defines the transmission band-width of the recording system, and E is a parameter characteristic of the apparatus and depending on the properties of the sensing device, the wavelength λ, and the magnitude of the illumination flux transmitted through the apparatus in the absence of a sample.

We now consider the usual case, where the width of the apparatus function is determined by the width of the slits, $\alpha = S$. Then (9) may be written in the

(10) $$\frac{\overline{\Delta\varphi^2}}{I^2} = \frac{U}{yz^4},$$

where $U = \frac{E\nu}{\gamma^5}$.

Substituting (7) and (10) in (8), we find

(11) $$F^2 = \frac{\overline{\Delta D^2}}{D^2} = M(x)\left[(az^2 + by^2)^2 r^2 + \frac{U}{x^2yz^4}\right]$$

To obtain the optimal conditions for measurement it is necessary now to find the values of x_m, y_m, z_m, which minimize F^2. We note that there is no minimum in ν, since only the systematic error depends on ν, and does so monotonically. Hence we will look for the minimum of F^2, considering

a, b, r, γ, v, and U, to be constants determined by the apparatus and the conditions of the problem. The question of the choice of x_m was analyzed in reference [1]. From these latter results we see that for our case one may take $x_m \approx 0.5$. The condition for the minimum

$$\frac{\partial F^2}{\partial y} = \frac{\partial F^2}{\partial z} = 0 \text{ gives}$$

$$\left.\begin{aligned} 2r^2(az^2+by^2)\,2az &= \frac{4U}{x^2y^2z^5}, \\ 2r^2(az^2+by^2)\,2by &= \frac{U}{x^2y^2z^4}. \end{aligned}\right\} \tag{12}$$

whence

$$y_m = \frac{z_m}{2}\sqrt{\frac{a}{b}} \tag{13}$$

or

$$\tau_m v = \frac{S_m}{2}\sqrt{\frac{a}{b}}, \tag{14}$$

$$z_m = \left(\frac{\delta E v}{5\gamma^5 a^2 r^2 x_m^2 \sqrt{a/b}}\right)^{1/9}$$

and for $x_m = 0.5$

$$F_m^2 = 13.35\,a^{8/9} b^{2/9} r^{10/9} \left(\frac{Ev}{\gamma^5}\right)^{4/9} \tag{15}$$

We note first of all the fact that for the optimal conditions, z_m and y_m must be related by the condition (13), which depends only on the form of $A(\omega)$ and $K(\omega)$. It is easy to see that as a result of (13) we have

$$\frac{P_m(\text{syst. }\alpha)}{P_m(\text{syst. }\tau)} = \frac{az^2}{by^2} = 4 \tag{16}$$

i. e. under the optimal conditions the systematic error due to the apparatus function is 4 times larger than the error which enters because of the inertia of the recording system. This ratio is valid for arbitrary $A(\omega)$ and $K(\omega)$. Moreover, one may show that under optimal conditions the following relation is also satisfied:

$$\frac{F_m^2(\text{syst.})}{F_m^2(\text{rand.})} = \frac{5}{4}, \tag{17}$$

which is also independent of the form of the functions occuring in it.

We note that if we proceed from a given signal-to-noise ratio, as was done in [4, 6, 8, 9], then instead of (13), equation (10) would lead to $yz^4 = \text{const.}$, or $\tau S^4 = \text{const.}$ Obviously these results differ significantly from ours. Similarly a narrow line would have too great a systematic error and a wide line would have an unwarranted amount of noise, so that for this choice of conditions the total error would not be a minimum.

On the other hand, equation (16) shows that the assumption of a small systematic error in the scanning, made in [1, 2] in connection with the effect of the time constant, may be justified to a certain extent, since it is clear from formula (11) that for deviations from the optimum in the direction of the larger y, P^2 increases very rapidly (for very large y, P^2 increases as y^4), and for deviations in the direction of small y, P^2 increases considerably more slowly (for very small y, $P^2 \sim 1/y$).

Let us consider particular cases.

Let the inertial properties of the recording system be described in terms of an equivalent RC circuit with time constant τ. Then

$$K(\omega) = \frac{1}{1+i\omega\tau v} \approx \left(1 - \frac{\tau^2 v^2 \omega^2}{2}\right)\exp[-i\omega\tau v], \tag{18}$$

$$b = \frac{1}{2} \qquad \kappa = \tau.$$

For the apparatus function of two slits of equal width we have

$$A(\omega) = \left(\frac{\sin\frac{\omega S}{2}}{\frac{\omega S}{2}}\right)^2 \approx 1 - \frac{S^2\omega^2}{12}; \quad \alpha = S; \quad a = \frac{1}{12}; \eta = 0. \tag{19}$$

If aberration is considered, one might expect that in this case $a(\lambda)$ would be approximately Gaussian. Then

$$a(\lambda) = \frac{2\sqrt{\ln 2}}{\alpha\sqrt{\pi}} \exp\left[-\frac{4\ln 2\,\lambda^2}{\alpha^2}\right], \tag{20}$$

$$A(\omega) = \exp\left[-\frac{\omega^2\alpha^2}{16\ln 2}\right] \approx 1 - \frac{\omega^2\alpha^2}{16\ln 2}; \quad a = \frac{1}{16\ln 2} \approx \frac{1}{11.1},$$

$$\eta = 0.$$

If we put $\alpha = S + c$ [1], where c is a small correction, then for the optimum we find

$$y_m = \frac{1}{2}\sqrt{\frac{a}{b}}\, z_m(z_m - g),$$

$$\frac{P_m(\text{syst.}\alpha)}{P_m(\text{syst.}\tau)} = 4\left(1 + \frac{c}{S}\right); \quad \frac{F_m^2(\text{syst.})}{F_m^2(\text{rand.})} = \frac{5}{4} + \frac{c}{S+c},$$

where $g = \frac{c}{\gamma}$.

In this case it would be difficult to derive the formulas for z_m and F_m^2. One may point out, however, that for $c \ll S$ the difference between

a Gaussian and a triangular apparatus function is very small, since for $S = \alpha$ the coefficients a are nearly identical.

From (13), (18), (19), we find for arbitrary $\varphi(\lambda)$

$$(21)\qquad y_m = \frac{z_m}{2}\sqrt{\frac{1}{6}} \approx 0.204\,\frac{S_m}{\gamma};\quad \tau_m v = 0.204 S_m$$

For a Gaussian function $a(\lambda)$, when $\alpha = S$ we would have $\tau_m v = 0.212 S_m$.

We will consider isolated lines of two types (Gaussian and dispersion) and will be interested in the measurement of the intensity at the maximum of the line, where φ'' is a maximum and hence the error in measurement will be greatest.

For lines with the Gaussian shape

$$(22)\qquad \varphi(\lambda)=\varphi_0 \exp\left[-\frac{4\ln 2\,\lambda^2}{\gamma^2}\right],\ \varphi''(0)=-\frac{8\ln 2}{\gamma^2}\varphi_0,$$

$$r = -8\ln 2;$$

and for lines with the dispersion shape

$$(23)\qquad \varphi(\lambda)=\frac{\varphi_0}{1+\frac{4\lambda^2}{\gamma^2}},\ \varphi''(0)=-\frac{8}{\gamma^2}\varphi_0,\quad r=-8.$$

In both cases γ is the line-width at half-maximum. From (14) and (15) we find for the Gaussian shape $\varphi(\gamma)$

$$(24)\qquad z_m=\frac{S_m}{\gamma}=1.61\left(\frac{Ev}{\gamma^5}\right)^{\frac{1}{9}},\ P_m=8.42\left(\frac{Ev}{\gamma^5}\right)^{\frac{4}{9}}$$

and for the dispersion shape

$$(25)\qquad z_m=\frac{S_m}{\gamma}=1.49\left(\frac{Ev}{\gamma^5}\right)^{\frac{1}{9}},\ P_m^2=12.7\left(\frac{Ev}{\gamma^5}\right)^{\frac{4}{9}}.$$

It would seem that to the extent that the shape of a single absorption band may vary between, roughly speaking, dispersion and Caussian, the formulae derived above allow one to estimate the optimum conditions for measuring the optical density at the line maximum for practically all bands. The changes in shape merely affect the coefficients in formulae (24) and (25), but the effect is not great.

Although all these computations have been made for absorption spectra, the results may also be applied to emission spectra if the slit is much narrower than the spectral line ($S \ll \gamma$). In this case the factor $M(x)$ does not occur in formulae (8) and (10), but this affects only the final expression for P_m^2. Formulas (13), (14), (16), and (17) are not changed. The applicability of these formulae to emission spectra depends only on the possibility of using equation (9). So long as $S \ll \gamma$, and (9) is valid, the results obtained above may also be used for emission spectra.

Using these results, we will now formulate recommendations concerning the choice of the conditions of measurement.

1. The line width γ and its form are estimated from preliminary measurements.

2. Knowing the characteristics of the apparatus a, b, and E and the scanning rate v and having estimated the value of r, one may use formulae (13) and (14) to find z_m and y_m and hence S_m and τ_m.

3. The accuracy of the measurement may then be estimated from formula (15).

One should note that for a given apparatus, operating under optimum conditions chosen by the above method, the accuracy obtained will be determined by the quantity

$$U = \frac{Ev}{\gamma^5} = \frac{E}{t_0^4},$$

where $t_0 = \frac{\gamma}{v}$ is the time to scan the width of the line. The quantity U is, therefore, the relative random error in measurement which would be obtained on a given apparatus with slit widths $S = \gamma$ and with the time constant of the recording system $\tau = t_0$ equal to the time required to scan the width of the line. Hence for a given accuracy in the apparatus constant E and a given line width γ, the only way to change U and thus increase accuracy is to increase the recording time t_0, i.e. decrease the scanning speed. Formula (15) allows one to estimate the scanning speed for which one may obtain the desired accuracy of measurement.

In conclusion the author takes this opportunity to express his gratitude to P.A. Bazhulin, V. I. Malyshev and S. G. Rautian for very valuable discussions.

July 18, 1958

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REPORTS READ AT THE XII CONFERENCE ON SPECTROSCOPY

The XII Conference on Spectroscopy was held in Moscow from 19 to 26 November 1958.

1500 persons participated, of whom 950 were from other cities. Among them were physicists, chemists, and many engineers, heads of factory laboratories. Guests from the Polish People's Republic were also present. Unlike previous conferences, the XII Conference was devoted to questions of applied spectroscopy and spectral analysis. At the 7 plenary and 18 sectional sessions 168 reports were read and discussed. In the mornings the work of the Conference was done in three sections - two on atomic and one on molecular spectroscopy - and in the evenings, in plenary sessions.

After an introductory speech by the chairman of the Spectroscopy Commission, S. L. Mandel'shtam, at the first plenary session, V. V. Voevodskii and L. A. Bliumenfel'd read a report on "Radiospectroscopy and Its Possibilities". The reporters indicated in concrete examples the possibility of using radiospectroscopy to study the structure of materials and for analytic purposes. Second was a report by L. V. Lipis "Spectral Analysis of Pure Materials". The reporter pointed out the importance of spectral analysis in nuclear power engineering, the semiconductor industry, the electrovacuum industry, and other branches of new technology. In the remaining six plenary sessions, the reports of V. M. Chulanovskii, P. A. Bazhulin and M. M. Sushchinskii, B. S. Neporent, and others, were read and discussed. In addition to these reports, there were five lectures by V. K. Prokof'ev, M. L. Veingerov and others, dealing with various aspects of applied spectroscopy. The purpose of the lectures was to assist fellow workers in factory laboratories and branch institutes in their practical work.

In the sessions of the two atomic spectroscopy sections, the participants concentrated their attention on the following:

Photoelectric Methods of Spectral Analysis. Ten reports were given dealing with matters in this area. Broad perspectives were outlined relating to the use of photoelectric methods in automation of industry, in carrying out continuous control of the chemical composition of materials, in regulating technological processes, etc. All this requires improving photoelectric methods and rapidly putting them into practice.

Quantitative Methods for Spectral Analysis of Very High Absolute Sensitivity (10^{-7} - 10^{-8} %). Five reports dealt with this question.

Detection of Gases in Steels and Certain Other Alloys. Seven reports dealt with this question.

Methods of Spectral Analysis Which Would Assure Rapid and Reliable Identification of the Composition of Geological Samples. Twelve reports on this question were read and discussed. It was noted that the next task is a further increase in the sensitivity and accuracy of the analysis of geological objects.

Standards for Spectral Analysis. Five reports were devoted to the question of establishing continuous manufacture of high quality standards.

Photographic Methods of Recording Spectra. In spite of the development of photoelectric methods, there is still a need for refinement of existing photographic methods which will be important for a long time yet, and will play, as before, a role in all analytical work conducted in industry. Twenty-one reports were devoted to this question.

In the molecular spectroscopy sections, the reports were devoted primarily to the following:

Molecular Absorption Spectra in the Infrared, Visible and Ultraviolet Regions; also Raman Spectra. Sixty-five reports on this question were read and discussed.

Spectral Apparatus. This question was considered in 13 reports.

Paramagnetic Electron and Nuclear Resonance. In recent years in the U.S.S.R., there has begun broad development of work in paramagnetic electron and nuclear resonance in general and their analytical applications in particular. Ten reports were devoted to this question.

At the conference there was a display of posters, diagrams, drawings and various kinds of accessories for the equipment and apparatus which make the work of spectroanalysts rapid and efficient. The display, containing about 40 exhibits, was a great success with the participants of the Conference.

With the consent of the Spectroscopy Commission of the Academy of Sciences of the USSR, the text of part of the reports of the Conference is printed in the current issue of the journal "Optics and Spectroscopy". (OiS). The text of the remaining reports will be published in the "Bulletin of the Academy of Sciences of the USSR", Physics Series, (IAN USSR FS), and in the journal "Factory Laboratory" (ZL).

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Rotational Spectrum of Water Vapor and the Absorption of Humid Air in the 40 - 2500 μ Wavelength Region

N. G. IAROSLAVSKII, A. E. STANEVICH

At the present time, experimental data are lacking in the literature on the pure rotation infrared spectrum of H_2O vapor in the wavelength range greater than 1400 μ*. Meanwhile, the presence of an absorption band at 1.63 mm (1630 μ) and the corresponding transition $2_2 \rightarrow 3_3$ (6.13 cm^{-1}) should be expected in the water vapor spectrum from the values of the rotational terms of the H_2O molecule calculated by Benedict and his colleagues [2]. This band has actually been detected, however, only by using microwave spectroscopy [3] and not in the infrared spectrum.

In the literature information is also lacking which could serve as an experimental confirmation of the presence of a broad transparent region, with a maximum at about 1.5 mm (1500 μ) in the infrared absorption spectrum of the atmosphere, as has been established by the theoretical investigations of Van Vleck [4].

The problem herein is to obtain additional experimental data on the longwave infrared spectrum of water vapor, especially in the wavelength range from 1400 - 2500 μ (i.e., in the 7.15 - 4.0 cm^{-1} wave number region), and also to obtain information on the absorption of air in the atmosphere in a very broad section of the infrared spectrum (from 40 μ to 2.5 mm) and to prove directly the presence of a transparent region in the atmosphere with a maximum at about 1.5 mm.

EXPERIMENTAL

The spectra in the 40 - 2500 μ region were obtained by using a vacuum longwave infrared DIKS-1 spectrometer which we had developed earlier [5-7]. In order to study the region 40 - 2500 μ, six echelettes of 270x270 mm with the constants: 0.083(3); 0.166(6); 0.50; 1.50; 2.50 and 5.00 mm, were used in the first order. A PRK-4 mercury lamp was the radiation source and an OAP-1 optico-acoustic receiver with a quartz crystal window was the detector.

An EPP-09 electronic potentiometer connected to the output of the main electronic amplifier was used to record the spectra. Depending on the region of the spectrum to be recorded and on the required value of the signal-to-noise ratio, the scanning rate of the spectrum ν and the time constant of the detection-recording system τ were selected so as to guarantee the required accuracy of the measurement of the wave numbers ν ($\Delta\nu \approx 0.02$ cm^{-1}) and of the transmissivity T ($\Delta T = 3 - 5\%$). For example, ν and τ would have the limiting values, 0.03 cm^{-1}/min and 200 sec, respectively, for a spectrum tracing in the 1200 - 2500 μ region. Hence the maximum signal-to-noise ratio would be 50 and the conditions for the accuracy of the measurements of ν and T would be satisfied.

*We investigated the rotational spectrum of the water molecule in the 1400 μ region in detail before [1].

The energy of the spectra of high orders of the echelettes and the scattered shortwave radiation were eliminated by means of selective modulation of the light flux and also by using various combinations of reflecting and transmitting filters. For example, when working in the 1200 - 2500 μ region, the radiation modulated by a KBr (or CsI) crystal first fell on the entrance slit of the monochromator and then into the receiver, was reflected twice from two echelette filters with the constants 0.85 mm, and then passed through 1 mm thick polyethylene and quartz crystal plates which had been strongly smoked by turpentine black and through an 0.13 mm thick glass plate. The filter combinations were different for the other, more shortwave portions of the spectrum. The presence of shortwave, scattered radiation in the blaze regions of the echelettes did not exceed 3 - 5%, i. e., the error in the measurements of the transmissivity. Scattered radiation was practically absent outside the blaze regions.

RESULTS

Shown in figure 1 is the absorption curve (II) of a 7.5 m long path of room air for a relative air humidity of 60% and 20° C which was obtained on the DIKS-1 instrument in the 1000 - 2500 μ region of the spectrum. Curve I is the energy distribution of the PRK-4 lamp, recorded by the instrument for the same optical path length (7.5 m) but after the instrument had been evacuated to a pressure less than 1 mm Hg. The conditions for recording both spectra were identical, as indicated in the legend to the figure.

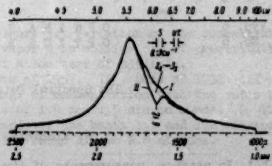

Figure 1. Tracings of spectra obtained on the DIKS-1. I - Energy distribution of the PRK-4 mercury lamp. II - Absorption curve of air. Echelette constant 5.00 mm.

A comparison of curves I and II clearly discloses the presence of absorption band of air in the atmosphere in the spectrum at 1634 μ. This band undoubtedly belongs to water vapor found in room air and corresponds to the transition $2_2 \rightarrow 3_{-2}$ (6.12 cm^{-1}) between the rotational levels of the H_2O molecules whose energies were computed by Benedict [2]. In passing let us note that this band was observed in the microwave spectrum at 1628 μ (6.14 cm^{-1}) according to the data of King and Gordy [3]. Let us call attention to the

absence of appreciable absorption of atmospheric air in 1200 - 2500 μ region of the spectrum in figure 1, which indicates the high transparency of the atmosphere in this portion of the spectrum.

The results of investigating the transparency of atmospheric (room) air in a wide range of the longwave infrared spectrum from 40 - 2500 μ are presented below. Tracings of separate portions of the absorption spectrum of humid air with 7.5 m path length and a 740 - 760 mm Hg pressure were recorded in these investigations on the DIKS-1 instrument with different echelettes, filters and under optimum conditions.

Presented in figure 2 are the results of converting all the spectra obtained in the 40 - 2500 μ region to values of the optical density D for a 10 m path length of room air at 20° C, 760 mm Hg pressure and a 60% relative humidity (specific water content ρ_{H_2O} = 10.5 g/m3).

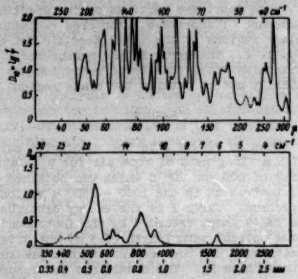

Figure 2. Optical density of air in the 40 - 2500 μ region.

As is seen from figure 2, the spectral behavior of the optical density discloses three regions of elevated transparency of atmospheric air: The 350 μ region, the region with center at 1300 μ and a wide transparency region extending from 1700 μ to the wavelength we investigated, 2500 μ. It should be noted that the relative error in determining the optical density in the last two regions of air transparency was significant and exceeded the quantity being measured by several times. Consequently, the thickness of the absorbing air layer must be enlarged ten- or hundredfold in order to determine more exactly the absorption of atmospheric air in these sections of the spectrum.

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The Spectral Determination of Water Vapor in the Upper Atmosphere

M. S. KISELEVA, B. S. NEPORENT AND V. A. PURSENKOV

1.) In essence, measurements of the moisture content of the layers of the upper atmosphere are bound up with the substantial role which water vapor plays in the radiation balance of the earth and in a number of other geophysical processes and phenomena. Even so, the distribution of water vapor concentration in the upper troposphere and stratosphere has not been investigated in sufficient detail up to the present. Low values of water vapor concentration and lov temperatures in the region of measurement define the difficulties in measurements of this kind. The few measurements of moisture in the upper layers of the atmosphere made up to now used, basically, methods based on the determination of the dew point [1-4] and the electrical conductivity of special electrolytic cells [5]. Some uncertainty in the results obtained obliged application of new spectral methods, in particular. The first experiments in this direction were made by the authors of this communication [6] and by Gates [7] where the absorption of infrared solar radiation by water vapor was measured. Recently a communication [8] has appeared concerned with the utilization for analogous purposes of the solar radiation in the Lyman-α region (1230 Å).

2.) Measurement of the concentration of water vapor by means of absorption in the infrared region is hindered by the existence of fine structure in the absorption spectra, which is not resolved by the usual spectrometers. The laws of absorption here are extremely complicated (see, for example [9-11]). In our laboratory [12] studies were made of the absorption of water vapor in some ranges of concentration and pressures of gases with the aid of an absorption spectrometer of high resolution, which demonstrated the possibility of using for purposes under consideration the square root law in its simple form $A = 1 - \frac{I}{I_0} = k\sqrt{lp^a}$,

where A is the absorption function, I_0, I, intensity of the incident and transmitted rudiation, l the quantity of precipitated water, p is the total pressure of the mixture (water vapor plus diluting gas), k and a are constants.

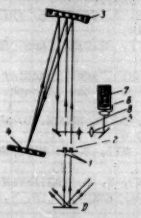

Figure 1. Plan of the instrument. 1.) Entrance Slits 2.) Filters. 3) Auto-collimating mirror. 4) Diffraction grating. 5. 6.) Lenses 7.) Radiation detector 8.) Exit Slit. D) Matte plate

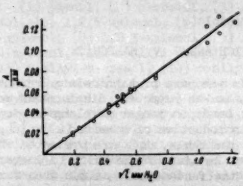

Figure 2. Dependence of the derived absorption function A on the square root of the quantity of precipitated water. p is the total pressure of water vapor and diluting gas.

The second complication of a general nature is associated with the existence of water in the atmosphere not only in the form of vapor, but also in the condensed state (liquid water, ice). In this connection, it should be voted that a method of infrared absorption measurement opens up, in principle, the possibility of an independent determination of the water content in all its states since the appropriate absorption bands are somewhat displaced in the spectrum.

3.) Our diffraction grating spectrophotometers were constructed with the intention of determining the water content at various altitudes, using the weakening of solar radiation in the water absorption bands at 1.4, 1.9, 2.6 microns. Parts of the spectrum at 1.2, 1.5 and 2.2 microns outside of the absorption bands are used for control wavelengths. Successive scanning of the wavelength regions is produced by using a multi-step cam which is connected to the commutator of a telemetry channel by which the data from the equipment are transmitted to the earth during the free flight of the balloon. The optical signals are modulated at a frequency of 100 cps. A photo-conductor of lead sulfide served as the radiation detector.*

The improved equipment used in recent work is substantially lightened; the working scheme is shown in Figure 1. The matte aluminum plate D is used as an illuminator; in order to facilitate the separation of the spectral orders in the equipment two entrance slits are provided which supply the appropriate shutters and filters. The remaining details of the scheme are evident from the figure. A modification of this equipment might be used for the investigation of the possibility of a separate determination of gaseous water, liquid water drops, or finely dispersed ice.

The instrument was calibrated by means of multipath cells constructed in our laboratory. The optical path lengths varied from 8 to 100 meters, the water vapor pressure from 0.9 to 10 mm Hg. The calibration ranges were chosen appropriate to the conditions of equipment operations at great altitudes. A sample calibration curve for the part of the spectrum near 1.4 microns is shown in Figure 2.

4) Flights were made from the bases of the Central Aerological Laboratories in the areas of Khar'kov and Moscov. After ascent to maximum altitude and a brief period of drift the equipment was released from the automatic balloon and recovered by parachute.

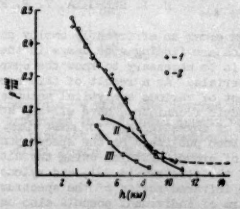

Figure 3. Variation of the concentration of water vapor p in millimeters of precipitated water against kilometers of altitude.
I - Data of 1957. II - Data of 1956. III - Data of 1955.
1--Change of concentration with the ratio of the signals of 1.4 and 1.5 micron bands. 2--The ratio of signals of the bands 1.4 and 1.2 microns; dotted line, the ratio 1.9 to 2.6 microns.

During the flight information was received about the attenuation of solar radiation at different altitudes, on the basis of which with the help of the calibration curves the water vapor concentrations represented in Figure 3 were calculated. Measurements of the moisture content by using the 1.4 micron band are successful up to about 11 kilometers; at greater altitudes use is made of the stronger 1.9 and 2.6 micron bands. Because of the complexity of the device in the flights of 1957, there is no hope of reliance on the data for the altitudes 11-14 kilometers. Our data are consistent with the results of other authors in the general behavior of the curves and the measured quantity of moisture.

*The photoconductors were furnished us by S. P. Tibilov and I. G. Kopilevich. We use this opportunity to express our gratitude to them.

In conclusion, the authors wish to express their profound gratitude to G. I. Golyshev, V. G. Kastrov, A. S. Nasenkis and I. V. Patalakhin for valuable assistance in the conduct of the work at the Central Aerological Observatory. (TsAO).

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Ultraviolet Absorption Spectra of Phenols

N. I. SHERGINA, V. P. KUZNETSOVA, A. S. NAKHMANOVICH AND I. V. KALECHITS

In order to efficiently employ phenolic mixtures which are finding wide usage in the national economy, it is necessary to know the composition of these materials. As a result of this need, the development of various analytical methods, including spectroscopic techniques, have already attracted the attention of investigators for some time. At present, work has been published on the spectrophotometric analysis of cresol mixtures using the ultraviolet region of the spectrum [1, 2], and xylenol mixtures using the infrared region of the spectrum [3,4]. The spectra of individual phenols also have been employed for the identification of pure compounds separated from mixtures.

Because of the latter investigations, there are available in the literature data on the absorption spectra of twenty-two (22) phenols [5,6] . In this laboratory a quantitative method for the determination of the composition of C_6-C_8 phenolic mixtures has been worked out [7], and, in order to undertake the development of a method for the analysis of phenols containing longer side chains, some C9 and higher phenols have been synthesized and studied. Thus, experimental data now has been accumulated on the absorption spectra of thirty-one (31) phenols (fig. 1), and a correlation of this information has allowed us to make some generalizations concerning the influence of substituents on the position and intensity of absorption bands of phenol derivatives.

EXPERIMENTAL

Measurements were carried out on an SF-4 quartz spectrophotometer. Optically pure isooctane was employed as the solvent. Purity of the samples was confirmed by determination of their physical constants.

In the majority of spectra the absorption maxima occurred at 271, 272, 278, 279, 284 and 285 mμ. In the case of naphthols and tetrahydronaphthols, as was expected, displacement of the absorption bands to longer wavelengths resulted from the introduction of a second ring [8] .

In the table, data are presented which demonstrate the size of the shift to longer wavelengths of the fundamental maximum when various substituents are placed in the ortho, meta, and para positions.

Introduction of methyl, ethyl, propyl and allyl groups into the position ortho to the phenolic hydroxyl group leads in all cases to a very small and nearly equal bathochromic effect. Substitution of the very same alkyl side chains in the meta position may increase, somewhat, this bathochromic shift. The greatest bathochromic effect occurs when alkyl substituents are introduced into the para position. The very same displacement also has been found during the substitution of alkyl groups on ortho, meta, and para cresols.

Thus, the length of chain branching in the substituent or the presence of a double bond does not have an important influence on the electronic absorption spectra, while the type of group changes both the form and position of the absorption bands.

A comparison of the absorption maxima of phenol, dihydroxy-and trihydroxy-phenols shows that introduction of the first hydroxyl causes a bathochromic shift. The substitution of a second hydroxyl group also results in a bathochromic effect, which is especially significant in cases of para substitution, while introduction of a third hydroxyl group produces a hypsochromic effect. The size of the displacement to the longer wavelengths, resulting from substitution of a hydroxyl group, greatly surpasses in all cases the corresponding shifts caused by introduction of alkyl substituents.

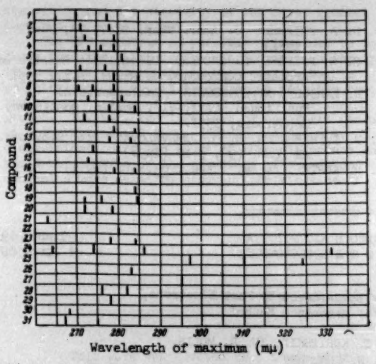

Figure 1. Displacement of absorption band maxima of phenol and phenolic derivatives.

Compounds: (1) phenol, (2) o-cresol, (3) m-cresol, (4) p-cresol, (5) 1,2,5-xylenol, (6) 1,2,6-xylenol, (7) 1,2,4-xylenol, (8) 1,2,3-xylenol, (9) 1,3,5-xylenol, (10) 1,3,4-xylenol, (11) o-allyl-phenol, (12)p-allyl-phenol, (13) p-allyl-m-cresol, (14) o-allyl-m-cresol, (15) 3,5-diethyl-phenol, (16) p-propyl-m-cresol, (17) o-propyl-m-cresol, (18) 2,4,5-trimethyl-phenol (19) p-ethyl-phenol, (20) o-propyl-phenol, (21) p-phenyl-phenol, (22) p-benzyl-phenol, (23) p-isobutyl-phenol, (24) β -naphthol, (25) α -naphthol, (26) tetra-hydro- β -naphthol, (27) hydroquinone, (28) resorcinol, (29) pyrocatechol, (30) pyrogallol, (31) phloroglucinol.

If vibration of the π-electrons of the benzene ring is considered to give rise to the electronic absorption spectra, it is evident that displacement of the electrons in the ring (fig. 2) will lower the energy of these vibrations, causing the frequency of the absorption band to be lowered and the wavelength to be increased. Since hydroxyl groups have four unshared electrons, while methyl (alkyl) groups have only σ -electrons, the former produces a significantly greater shift of the electron density in the benzene ring, which results in a greater magnitude of the bathochromic effect.

The larger bathochromic effect resulting from introduction of a second substituent in the para position as opposed to the meta and ortho positions may be explained by features of the benzene ring (the so-called benzenoid structure), which allows, in most cases, the mutual influence of two groups to be particularly easily transmitted in the para position.

The significant hypsochromic shift which occurs upon introduction of a third hydroxyl group may be explained best by a change of structure and configuration of the bonds. It is well known that polyhydric phenols can partially exist in the keto form and that the concentration of this configuration increases when a larger number of hydroxyl groups are present. Thus, phloroglucinol frequently reacts to give derivatives of the keto form (fig. 3).

Displacement of absorption bands upon introduction of substituents.

Original Compound	Substituents Introduced	Shift (mμ)
(a) Ortho Substitution		
phenol	CH_3	+1, +0.8
	C_2H_5	+1, +0.8
	C_3H_7	+2, +1.2
	$CH{=}CH_2$*	+2, +0.8
	OH	+8
o-cresol	CH_3	0, −1
m-cresol	CH_3	+2, 0
	C_2H_5	+2, +1
	$CH{=}CH_2$*	+2, +1
p-cresol	CH_3	0, 0
pyrocatechol	OH	−10
(b) Meta Substitution		
phenol	CH_3	+2, +1.8
	C_2H_5	+2, +1.8
	OH	+6, +4.6
o-cresol	CH_3(1,2,3)	+3, +1
m-cresol	CH_3(1,2,5)	+1, +2
p-cresol	CH_3	+1, +2
resorcinol	OH	−1, −1
		−9
(c) Para Substitution		
phenol	CH_3	+8, +7.8
	C_2H_5	+8, +7.1
	OH	+25
	$CH_2{-}CH{-}CH_3$ (with CH_3)	+8, +8.4
o-cresol	CH_3	+8, +7
m-cresol	CH_3	+6, +5
	C_2H_7	+6, +5
	$CH{=}CH_2$*	+6, +4

* Translator's note: The starred structural formulae presented in the table appear to be incorrectly type-set as they undoubtedly should represent allyl groups ($CH_2CH{=}CH_2$).

Figure 2

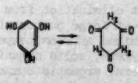

Figure 3

Since both pyrogallol and phloroglucinol, which give evidence of a hypsochromic shift in comparison with the corresponding dihydric phenols, still possess absorption bands characteristic of phenols these compounds very likely exist as a mixture of the two tautomeric configurations. The important differences noted in the positions of absorption bands of para isomers with respect to ortho-meta isomers has allowed us to conclude that spectrophotometric methods of analysis might be used effectively for the study of the composition of phenolic mixtures in those cases where the components differ by a number of para substituents. This occurs in cases such as meta-para cresol mixtures, mixtures of 3- and 4-ethyl phenols, 1,2,4- and 1,2,5-xylenols, and others.

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Investigation of Free Radicals Formed by Bombardment by Fast Electrons, by the Electron Paramagnetic Resonance Method

N. IA. BUBEN, V. V. VOEVODSKII, A. T. KORITSKII, IU. N. MOLIN, I. I. CHKHEIDZE AND V. N. SHAMSHEV

The electron paramagnetic resonance (EPR) method opens up wide possibilities for the investigation of the kinetics of agglomeration, destruction and mutual transformation of radicals produced in various chemical compounds by the action of ionizing radiation. An apparatus was made up for recording EPR spectra directly during bombardment of the sample under investigation [1].

An EPR spectrometer with high-frequency modulation of the magnetic field, working at a frequency of approximately 9400 mc, was equipped with remote control which made it possible to work in a shielded room at a distance of about 10 m from the resonant cavity into which a beam of fast electrons was introduced.

The samples investigated were maintained at temperatures from -180 to +150° C. The dose magnitude in the samples could attain 10^6 - 10^7 R/sec and was limited in practice by the rate of heat elimination from the sample.

A large number of different materials were examined at room temperature, including a number of polymers, solid organic acids and their salts, and several aromatic compounds. In the majority of substances the radicals obtained turned out to be rather stable. Their lifetimes amounted to several hours, and in certain cases even more.

In going to lower temperatures we were successful in observing the characteristic lines of atomic hydrogen in the EPR spectra on bombardment of aqueous solutions of sulfuric acid and certain salts. The bombardment of several compounds at low temperatures and their subsequent recooling showed that a change in the type of the EPR spectrum frequently takes place here, which in some cases is of an irreversible nature (dicarboxylic acid, polyformaldehyde), and is reversible in other cases (capron).

The radicals in oxalic acid and polyethylene have comparatively small lifetimes and possess sufficiently simple spectra for carrying out kinetic investigations. In oxalic acid the paramagnetic absorption signal is a single line. After stopping the bombardment a decrease of the signal takes place at a rate which is essentially dependent on the temperature [2]. On replacing the ordinary hydrogen in oxalic acid by deuterium, a splitting of the absorption line is observed. This result signifies that the line width depends on the interaction of the unpaired electron with the magnetic moments of the protons. The EPR spectrum of irradiated single crystals of oxalic acid, in which a clear picture of the hyperfine structure is observed at a definite orientation of the crystal in a magnetic field, also bears this out. The spectra of aqueous and anhydrous oxalic acid do not differ from each other. This proves that the observed spectrum is not related to the presence of the water of crystallization. Apparently, it is due to a radical of the type $R - C\langle^{O}_{O}$, formed as a result of breaking off a hydrogen atom from the carboxyl group. Paramagnetic absorption signals analogous to the signal in oxalic acid, are also present in the fairly complex spectra of other organic acids, which is an additional argument in support of the assumption expressed about the nature of the radical. Measurements of the kinetics of the relaxation of the EPR signal in oxalic acid at room temperature show that the disappearance of the radicals is described by the equation $\frac{dn}{dt} = -Kn^2$. At 25° C the reaction rate constant for the destruction of the radicals is, according to our estimate $K=10^{-21}$ cm^3/sec. The quadratic concentration law for the destruction of the radicals is confirmed by measurements of the stationary concentration of radicals as a function of the dose magnitude W. It turns out that $n_{sta.} \sim \sqrt{W}$.

The presence of water of crystallization essentially changes the conditions for the destruction of the radicals: the quantity K turns out to be larger in the anhydrous acid than in the aqueous.

By bombarding polyethylene we were successful in recording at room temperature the radical CH_2-CH-CH_2, which is stable at low temperatures [3]. The change of the EPR spectrum of bombarded polyethylene shows that a transition of the first radical into the second, more stable radical takes place, where the rate of this reaction decreases with a decrease in temperature. It is interesting to note that in two samples of polyethylene differing in their method of production, the rate of this

transition and the stability of the first radical turn out to be different.

The EPR spectrum of paraffin allows one to conclude that the first radical formed in it under the influence of bombardment is the same as that in polyethylene, i. e., it is connected with the breaking off of an atom of hydrogen from one of the methyl groups. However, the lifetimes of the first radical in polyethylene and in paraffin are different. For a clarification of the cause of this difference and the determination of the structure of the second radical a more detailed study of the kinetics of destruction of the first radicals and their transition to the second will be undertaken, together with a comparison of the EPR spectra of various hydrocarbons.

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Study of α- and β- Spodumenes by Infrared Spectroscopy

L. A. IGNAT'EVA

This work was devoted to a study of the infrared absorption spectra of α- and β-spodumenes with the aim of clarifying the structural changes that take place on transition from the α- to the β-phase.

α-spodumene is a natural mineral $LiAl[Si_2O_6]$ containing approximately 65% SiO_2, 27% Al_2O_3, 7% Li_2O, and various impurities. When it is heated to a temperature of the order of 1000°C it goes over into a new phase called β-spodumene [1]. The transition is endothermic, and is accompanied by a large increase in volume. Many physical constants, such as the specific gravity, refractive index [1,2], the distance between surfaces in the Debye crystallogram*, and so on, change sharply on a transition from α-spodumene to β-spodumene (see Table).

Physical Constants of Spodumenes

Substance	Hardness	Specific Gravity	Index of Refraction
α-spodumene	6.5 – 7	3.13 – 3.20	1.66
β-spodumene		2.3	1.52-1.53

All this indicates that in the α→β transition there is a sharp change in the lattice itself.

α-spodumene has a chain structure and is similar to clinoenstatite, having an atom of Al and an atom of Li in place of two atoms of Mg, surrounded by six atoms of O (the coordination number of the Al being 6) [3,4]. The crystallographic structure of β-spodumene has not been deciphered. On the basis of certain physical properties of β-spodumene (specific gravity, index of refraction, and other properties) the hypothesis has been made that β-spodumene is a body-centered silicate, where the aluminum is inside a tetrahedron, that is, surrounded by four atoms of O (the coordination number of the Al being 4).

It was desirable to apply the method of infrared spectroscopy to clear up the question of what changes take place in spodumene upon transition from the α- to the β-phase. The infrared spectra were measured in the double-beam infrared spectrometer model IKS-2 in percent transmission in the range from 550 to 3000 cm-1. In order to investigate the transition from α-spodumene to β-spodumene we used samples of spodumene subjected to different heat treatment in a hollow Silit furnace, in which the sample was held at a specified temperature for two hours. The samples used for measurement of the spectra were thin plates of spodumene, thoroughly ground in oil and deposited on a NaCl substrate.

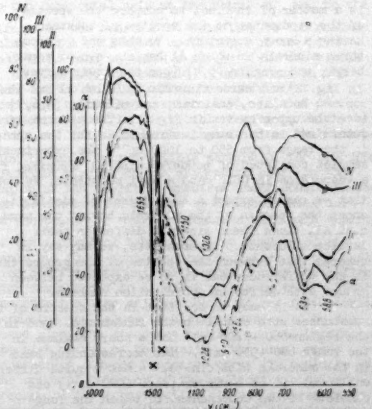

Figure 1. Infrared absorption spectra of spodumenes subjected to heat treatment at various temperatures, and the spectrum of α-spodumene not heat-treated
α-spectrum of α-spodumene, not heat treated; I -- 700°C; II--800°C; III--900°C; IV--1050°C. X--oil bands

Figure 1 presents the spectra of spodumenes heated to various temperatures, and the spectrum of α-spodumene not subjected to heat treatment. It is clear from the spectra that the spectrum changes sharply in the transition from α- to β-spodumene.

*The Debye crystallograms of α- and β -spodumene were obtained in a URS-70 apparatus with an RKD-62 camera.

Heating to 800°C changes the spectrum of α-spodumene only very slightly; but above a temperature of about 900° the spectrum is quite different. This indicates that the transition from α-spodumene to β-spodumene begins near this latter temperature. We shall consider the two limiting curves, the most characteristic spectrograms, namely that of the initial α-spodumene (the lowest curve) and that of β-spodumene (the upper curve, IV).

1) The broad absorption band exhibited by α-spodumene in the range from 1200 to 860 cm^{-1} a fundamental band appearing in the spectrum of all silicates--is much narrower in β-spodumene, appearing as a band ranging from 1150 to 1000 cm^{-1} and the intensity is diminished in this band. In α-spodumene the absorption is higher in the left portion of the band, (around 1100 cm^{-1}), whereas in β-spodumene it is higher in the right portion of the band (around 1026 cm^{-1}). 2) α-spodumene has two absorption bands, at 910 and 862 cm^{-1}. Both of these are absent from the spectrum of β-spodumene. 3) α-spodumene has a narrow band at about 740 cm^{-1}, but in β-spodumene the band is greatly broadened toward the high frequencies, evidently as a result of the development of a new absorption band in β-spodumene at about 765 cm^{-1}. 4) In the low frequency region α-spodumene has two strong absorption bands at 634 and 588 cm^{-1}. These bands disappear completely in the transition from α-spodumene to β-spodumene.

Insofar as we may postulate a change in the coordination number of aluminum (c.n.Al) in the transition from α-spodumene to β-spodumene, it is a matter of interest to compare the spectra of the spodumenes to the spectra of substances having a known structure. To this end we chose three minerals in which Al has the c.n.6: topaz, beryl, and cyanite [5,4] (see the lower curves in Fig. 2) and three minerals in which Al has the c.n. 4: sodalite, analcite, and milarite [4,6,7] (see the upper curves in Fig. 2). The spectra were determined in the same instrument as for the spodumenes in the range from 550 to 1600 cm^{-1}; the experimental samples consisted of powdered mineral deposited from a suspension in CCl_4 onto a NaCl substrate. We note that we cannot expect a high degree of similarity among the spectra of the minerals having the same c.n. Al, since these minerals differ in their lattice structure. Nevertheless, we may say in general that between the spectra of the groups there is the difference that is to be expected between groups with different coordination numbers.

It is easy to see that in the spectra of the substances with c.n.Al = 6 the fundamental band in the region 880--1200 cm^{-1} has a sharp maximum in the range 880--950 cm^{-1}. The corresponding band in the minerals with c.n. Al = 4 has a quite different form; it is narrower (1180-1020 cm^{-1}) and consists of two components, of which the long-wave component (1020-1040 cm^{-1}) is more intense. In the spectra of the substances with c.n.Al = 4 there is no band in the region 880--950 cm^{-1}, whereas this band is characteristic of substances with c.n.Al = 6. Moreover, in the spectra of substances with c.n. Al = 6 the bands in the region 590--680 cm^{-1} are very intense. Although the bands differ in form, they are comparable in intensity to the fundamental band in all three minerals. For substances with c.n.Al = 4, there are either no bands in this region, or bands that are weak compared to the fundamental. The above properties of the spectrum allow us to determine the c.n. of Al in any silicate.

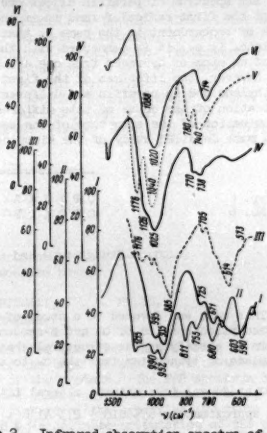

Figure 2. Infrared absorption spectra of minerals with coordination number of Al = 6(3 lower curves) and coordination number of Al = 4 (3 upper curves)

I--cyanite; II-- beryl; III--topaz; IV--analcite; V--milarite; VI--sodalite

If we now return to the spectra of spodumenes (Fig. 1) and compare them with the spectra of minerals having Al in six-fold and fourfold coordination, we find the following. The spectrum of α-spodumene has all the properties characterizing a mineral with c.n.Al = 6: its fundamental band has strong maxima in the region 860--910 cm^{-1} and very strong bands in the region 550--650 cm^{-1}. The spectrum of β-spodumene, on the other hand, is much like the spectra of substances having c.n. Al = 4. In fact, the fundamental band of β-spodumene is narrow and consists of two components, of which the more intense is to the right and has a maximum at 1026 cm^{-1}. The spectrum of β-spodumene has no band in the regions 860--910 cm^{-1} and 550--650 cm^{-1}. We may therefore take it as established that in the transition from α-spodumene to β-spodumene there is a change in the coordination number of Al. The Al atom moves from an environment of 6 atoms of O to an environment of 4 atoms of O, i.e. it occurs at the center of a tetrahedron, like the Si atom. This is evidently one of the basic factors causing a sharp change in the properties of spodumene in the α→β- transition, since it has been shown on the basis of experimental data that the coordination number has a strong influence on the properties of minerals [8]. The determination of the coordination number of aluminum by spectral analysis can, it would seem, be widely used and is applicable to a large number of silicates containing aluminum.

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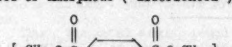
Reflection Spectrum and Optical Characteristics of Therilene in the 700 – 1300 cm^{-1} Region

L. D. KISLOVSKII

Quantitative measurements of the spectra of substances with intense absorption bands are made difficult by the necessity to investigate layers with thickness smaller than the wavelength. Thus, in the case of therilene one is forced to deal with layers whose thickness is of the order of magnitude of one micron [1]. In order to overcome these difficulties, a number of clever methods have been proposed [2, 3]. However, most promising, in our opinion, is the use of reflective spectrophotometry methods [4].

In the paper being presented, there is described an attempt to determine the optical characteristics of amorphous ("disoriented") therilene



(polyethylenterephthalate , used to produce synthetic wool) by reflection on the basis of a method we described earlier [5]. The method is related to conceiving and representing the individual bands on the basis of a model of resonators with damping, whose amplitudes and phases are considered as the amplitudes and phases of normal reflection.

The mirror reflection spectrum (fig. 1) has been obtained, for practically normal light incidence on the polished therilene plate, by using an IKS-11 spectrometer with an NaCl prism. A plate of crystalline KBr whose refractive indices are well known was the reflection etalon.

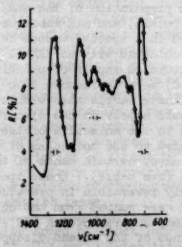


Figure 1.

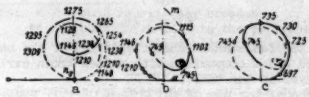


Figure 2.

A resonance circle [5] (see fig. 2.b) tangent to the horizontal axis at the point n_o and to the circle m was constructed according to the maximum value of the reflection coefficient of the given individual band to which a circle (see the circle m on fig. 2.b, for example) corresponds on the plane of the complex reflection coefficient and according to the known value 1.58 [6] of the refractive index in the visible region to which the point n_o (fig. 2.a) corresponds since the absorption is small in the visible portion of the spectrum. Resonance circles of the absorption bands in the region of the therilene spectrum under consideration can be constructed tangent to the horizontal axis at the point $n_o = 1.58$ because of the high quality of the individual bands [5]. The quality of the bands was found according to the values of the reflection coefficients and the frequencies at the reflection maximum and in a number of nearby points (where the effect of the adjacent bands is not felt), which permitted the values of the frequencies to be disposed along the resonance circle. Hence, because of the high values of the quality, the usual radio engineering reduced resonance curve [7] could be used. The spectral behavior of the reflection obtained because of this construction did not correspond to experiment where the perturbation of the adjacent band started to be felt, for example, at the longwave wing of the band (fig. 2.a).

Constructing, similarly, a resonant circle of the bands (fig. 2.b) and superposing the frequency scale along it, the vector displacements of corresponding points relative to their position on the circle (fig. 2.a) have been obtained for the frequencies of the longwave wing of the band (fig. 2.a). The spectral values of the reflection coefficient here agreed with experiments. The other reflection bands of the portion of the spectrum under consideration are treated by the same method, as is shown on

figure 2. Its three parts (a, b, c) have been separated for clarity but should have been superposed. The values of the optical constants in the 600 - 1300 cm^{-1} region found by connecting resultant points of the common resonance curve (solid line, fig. 2.a) with the grid coordinate n,k in this plane [5] are presented on figure 3.

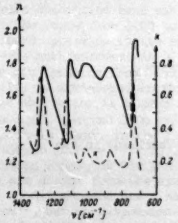


Figure 3.

The fundamental characteristics of the bands studied and a comparison with values known earlier are given in the table.

Hence, the use of the method of [5], permits the optical characteristics to be determined in the case of a complex spectrum of strongly-absorbent organic material.

Values of the Frequency (cm^{-1})			Quality $F(Q)=Q$	Vibration Characteristics[1]	
Reflection Peak Exper.	Absorption Peak Exp. [1]	Comp.		Corresp. to which Group	Vibration Character
1254	1265	1265	18.6	=O-O	Stretching Vibration
1101	1110	1115	18.6	-O-O	
1014	1120 1020	–	–		
840	875	–	–		
725	730	730	25		Bending Vibration

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Infrared Spectra of Sublimed Films of Metal Oxyquinolinates

A. N. SIDOROV

An investigation of the infrared spectra of metal oxyquinolinates was carried out for the purpose of determining the capability of a metal atom, which is bonded to the oxyquinolinate group of forming molecular complexes with foreign molecules--addends. Pyridine and hydrazine were selected as the addends, the molecules of which have atoms of nitrogen carrying a free pair of electrons which makes them capable of forming a coordination bond.

The spectra of the oxyquinolinates of different metals in the 650 - 5000 cm^{-1} region were studied earlier by Stone [1] and by Charles et al. [2]. In particular they showed that the spectrum of 8-oxyquinoline differs significantly from the spectra of metal oxyquinolinates. The spectra of oxyquinolinates differ insignificantly even in cases where the metal atoms have different valencies. The essential differences among the spectra of oxyquinolinates of different metals are observed only in the 700 - 900 cm^{-1} region. This was confirmed also by our measurements which were carried out in the 700 - 1800 cm-1 region for the special case of magnesium and aluminum oxyquinolinates atom disposal.

In obtaining the spectra of the oxyquinolinates in our work it was decided not to prepare the samples in the form of suspensions in liquid paraffin as was adopted in references [1] and [2] because the presence of the immersing medium would impede access of the addend molecules to the oxyquinolinate. The samples of the oxyquinolinates were prepared in the form of films sublimed in a vacuum on potassium chloride plates (sublimation takes place with sufficient speed in the temperature range of 270 - 300° C). The preparation of the samples, the scanning of the spectra, and all subsequent operations were performed in a special vacuum cell [3]. The spectra were obtained with an IKS-11 instrument.

If saturated vapors of pyridine or of hydrazine (at 20° C) were introduced into the cell with the oxyquinolinate sample then within 15 - 20 hours, weak bands would appear in the spectra of the sample corresponding to the molecules of the addend which have been bonded to the molecules of the oxyquinolinate; while, also, certain bands of the oxyquinolinate are displaced (see table). These spectral changes were completely reversible in practice; after vapors of the addend were pumped from the cell for an hour at a sample temperature between 150 - 180° C, the absorption bands of the addend disappear and the displaced bands of the oxyquinolinates returned to their original positions.

By a comparison of the spectra of the oxyquinolinate in vacuum and in the presence of the vapors of the addend it is noticed that in the case of the interaction of the oxyquinolinate with the addend, spectral changes were deleted for the most part, in the 700 - 900 cm^{-1} region (not taking into account the absorption bands of the addend)--i.e., just in that region where the greatest differences were observed among the spectra of the oxyquinolinates of different metals, Hence, the following conclusions may be drawn. The absorption bands in the 700-900 cm^{-1} region, which differ in the spectra of the oxyquinolinates of different metals, correspond to the vibrations of the oxyquinolinate molecule on which the metal atom exerts a direct influence. The fact that these bands were displaced during the interaction of the oxyquinolinate with the vapors of the addend permits us to contend that the molecule of the addend was bonded only to the metal atom in the oxyquinolinate molecule.

In the presence of water vapor, both under vacuum conditions and in air, the spectra of the oxyquinolinates of magnesium and aluminum reveal none of these changes. It is well-known, however, that in the preparation of magnesium oxyquinolinate according to Berg's method [4] the magnesium oxyquinolinate forms a dihydrate. A comparison of the spectra of the dihydrate and the anhydrous oxyquinolinate of magnesium, described in ref. [1], shows that the bonding of water, aside from the appearance of the wide bands around 3300 cm^{-1} corresponding to the bonded molecules of H_2O, gives rise to a strong decrease in the intensity of the absorption band at 731 cm^{-1}. From this we can conclude that the water molecules which form the dihydrate with magnesium oxyquinolinate are bonded to the metal atom, just as are pyradine and hydrazine.

Thus, the metal atoms, found in the structure of the molecules of oxyquinolinate, are capable of entering into a reversible interaction with molecules of addends, resulting in the formation of molecular complexes of oxyquinolinate-addend. The same characteristic is possessed by metal atoms in the phthalocyanide molecule [5] where the metal atoms are situated in the center of the tetrazopyrrole ring of conjugate bonds.

Comparison of the frequencies of the absorption band of the oxyquinolinates of magnesium and of aluminum in a vacuum and in the presence of vapors of the addend (in cm^{-1}).

	In a vacuum	In the presence of hydrazine vapor	In the presence of pyridine vapor
Oxyquinolinate of Magnesium	–	–	705(Pyridine)
	731	731	731
	788.0	790.4	790.6*
	805.9	802.7	805.1
	823.4	825.7	824.2
Oxyquinolinate of Aluminum	–	–	705(Pyridine)
	748	748	748
	787.6	791.3	785.0 and 790.3**
	805.9	803.8	805.1
	825.6	825.0	825.6

Note: * The band is slightly broadened.
** The band 787.6 cm^{-1} in the pyridine vapor is clearly divided into two bands

The author expresses deep gratitude to academician A. N. Terenin for his suggestions and under whose skillful guidance this work was accomplished.

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Determination of the Degree of Absorption of Analytical Lines in Arc and Spark Spectra

I. V. PODMOSHENSKII AND V. M. SHELEMINA

In measuring line absorption, two distinct light sources with identical properties are usually used. In the case of the arc and spark, large fluctuations of spectral intensity in time, and considerable shifts of sources in space, make it difficult to use this method. A version of the method, in which the illuminating source is replaced by an image reflected from a concave mirror makes it possible to attain an almost complete similarity of all properties of the two sources, including the time-dependent variation of intensity*. However, a concave mirror, by giving an inverted image, does not permit superposition of the corresponding zones of the source and its image.

An optical arrangement** which effects perfect superposition of corresponding zones is shown in figure 1.

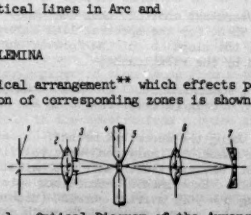

Figure 1. Optical Diagram of the Arrangement.

1 - Slit of the ISP-22 Spectrograph; 2 - Objective f=150 mm; 3 - Diaphragm; 4 - Electrodes; 5 - Arc; 6 - Achromatic objective f=75 mm; 7 - Concave mirror R=150 mm.

* The finite speed of light introduces only an insignificant (~ 10^{-9} sec.) delay into the intensity vs. time curve of the reflected source.

** At the tenth Conference on Spectroscopy, the report by Kondrasheva and Podmoshenskii briefly mentioned the use of this arrangement in the study of absorption.

Achromatization of objective 6 and coincidence of its center with the center of curvature of mirror 7 are essential. The suggested arrangement is free of vignetting of the light.

When the source is traversed by reflected rays, the increase in the intensity of the spectral line is governed not only by absorption by the source, but also by losses of light in mirror 7 and objective 6. Factors such as diaphragming of the beam by the electrodes or by the mounting of objective 2, which are difficult to control, can also have an effect. A relative method of measurement must therefore be used. For that reason, a small portion of the reflected beam is blocked off, and the occulter imaged sharply on the slit of the spectrograph. A wire fastened horizontally to the frame of objective 6 is conveniently used for that purpose. If a stigmatic spectrograph is used, two spectra appear on the spectrogram: at the position of the wire image — an emission spectrum of the source, and adjoining it — an emission spectrum of the source at higher intensity. In order to calculate the degree of absorption of a given spectral line, one merely compares the intensities of the line in these spectra.

Let I be the intensity of a given spectral line, p_λ – transmittance of the illumination system, p_λ I - intensity of this spectral line in the spectrum after passing through this system, and T the transmittance of the arc or spark.

The relative increase in the intensity of the spectral line will be

$$\frac{I + p_\lambda TI}{I} = 1 + p_\lambda T.$$

Using the photographic method of measurement,

$\lg (1 + p_\lambda T) = \frac{\Delta S}{\gamma}$, where ΔS is the difference in optical density of the spectral line with and without the reflected beam traversing the source. In multi-line arc and spark spectra, one can select weak lines for which (N.f.l) is so small that absorption in the discharge is almost zero, e.g. T=1. The intensities of these lines will increase to the maximum possible degree; since

$\lg (1 + p_\lambda T) = (1 + p_\lambda) = \frac{\Delta S_{max}}{\gamma}$, p_λ can be determined and, T thus computed.

Then, for the spectral line undergoing absorption, the slope b of the "growth curve" will be given by the relationship

$$b = \frac{\Delta \lg I}{\Delta \lg (N \cdot f \cdot l)} = \frac{\lg (1 + T)}{\lg 2}.$$

Using the described method, b was measured for a number of analytical spectral lines of Ni, Cr, Si, Mn, excited in an electronically regulated AC arc. Experimental conditions were: phase at firing $\varphi = 90°$; average current (according to ammeter) I = 4a, support electrode made of copper, shaped to a truncated cone; interelectrode gap = 2 mm; pre-burn = 10 sec; exposure time = 10 sec.

To avoid diaphragming, the arc was ignited on the side surface of cylindrical samples of steel. Standards of the V set of "IM steels and pure Ni were used. To determine $\frac{\Delta S}{\gamma}_{max}$ we chose weak lines corresponding to transit[illegible] high level: Fe_I 3411.35, Fe_I 3410.17 [illegible]oth[illegible]

The curves of b vs. concentration elements on the electrodes given in figure 2, [illegible] obtained by averaging the results of photom[illegible] of twenty spectra. At low concentrations b=1 in all curves. This result confirms the absence of noticeable absorption in lines chosen for determining $\frac{\Delta S_{max}}{\gamma}$; if there had been absorption, the measured value of b would have been greater than one.

Over a relatively narrow range of concentration, b decreases from 1 to 0.5. In this region, one should apparently encounter curved analytical curves (intensity vs. concentration). On further increasing concentration to 100%, b remains approximately constant at b = 0.5, which corresponds to a dependence of the intensity of the spectral line on $\sqrt{N.f.l}$. The general behavior of b is well explained by the "growth curve" at values a > 1, and agrees with measurements by Dvornikova [1].

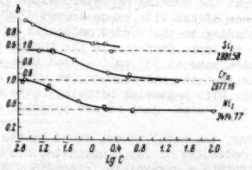

Figure 2. Curve b vs. concentration of Ni, Cr, Si, in electrodes.

Measurement of the absorption of lines of Ni and Cr in a high-voltage spark also indicated considerable absorption. The values obtained differ sharply from the values of b given by Fishman on the basis of indirect measurements. [2].

One must note that several reference lines used in spectral analysis, (Fe_I 2880.76, Fe_I 2936.9, and Fe_I 3413.13) also revealed considerable self-absorption.

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Low Voltage Pulse Discharge in Vacuo to Obtain Spectra

F. Z. PEDOS, N. S. SVENTITSKII, AND Z. I. SHLEPKOVA

The selection of vacuum sources of line spectrum is relatively small. Most often a "hot" spark [1] is used but it requires a rather bulky high voltage power supply. A "sliding" spark [2], set up when electrodes make contact with a semiconductor or dielectric, is of considerable interest, however, it is not always possible to introduce a foreign substance into the discharge.

Taking into account the simplicity of low voltage sources of light, it is interesting to obtain a discharge in vacuum by employing the principle of a separate supply [3].

The experiments we conducted have shown that this is possible. Without any difficulties, a pulse flash occurs when an insulator is introduced into the interelectrode space, and an incendiary high-frequency spark slides along it (Fig. 1, A). But, here, in addition to the spectrum of the electrodes there appears the spectrum of the insulating gasket.

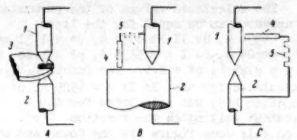

Figure 1. Diagrams of electrode connections. 1 - 2 - main electrodes; 3 - porcelain disc with a cutout; 4 - auxiliary electrode; 5 - Ohmic resistance. For meaning of A, B, C, refer to the text.

Without the porcelain plate one can obtain ignition of the discharge if the usual high frequency generator is used for the ac arc, but only for small interelectrode spacings (approximately 0.2 mm). Spark gap restriking did not occur without replacement of the electrodes, because after the powerful pulse, the interelectrode spacing increased and, therefore, the gap. However, use of an auxiliary electrode (Fig. 1, B and C) [4] enabled us to obtain a pulse discharge for interelectrode spacings greater than 5 mm and to repeat it with the same electrodes many times. Arrangement B (Fig. 1), where one of the electrodes has a rather large flat surface, is convenient; if both of the electrodes are of the same diameter, it is worth while to arrange the auxiliary electrode as shown in figure 1, C. Electrode 4 can be either carbon or metallic.

The experiments were conducted in a vacuum of $10^{-4} - 10^{-5}$ mm. of Hg, and pulse flashes were obtained from a 5 to 50 thousand μF bank of capacitors. The discharge was started at the auxiliary electrode 4 (Fig. 1, B), and jumped over to the main gap 1-2, with most of the energy being emitted from the latter. This was confirmed by observing considerable destruction of the electrodes at the main gap and hardly noticeable destruction at the auxiliary one.

In obtaining the spectra (using a DFS-6 [5] vacuum spectrograph) from the discharge of a large capacitance (approximately 50,000 μF) a very heavy destruction of the electrodes and a visible deposit of metal on the slit of the spectrograph were observed. It is more expedient to use less intense flashes (from a capacitance of between 5,000 – 8,000 μF) repeated many times (100 – 200 times). Therefore, the pulse generator circuit [4] was modified (Fig. 2) in such a way that the flashes were automatically repeated the desired number of times at a constant voltage.

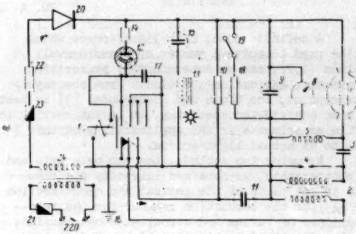

Figure 2. Diagram of the low voltage generator.

1 - relay RS-13; 2 - ignition coil TATE, B-26 v; 3 - high voltage capacitor 100 pF; 4 - auxiliary discharge gap; 5 - induction coil; 6 - analytic gap; 7 - vacuum container; 8 - voltmeter; 9 - bank of electrolytic capacitors 1 to 50 thousand μF; 10 - 5.4 kΩ resistor, 2W; 11 - electrolytic capacitor 20 μF, 450V; 12 - gaseous regulators SG-4S and SG-20; 13 - electromagnetic counter; 14 - 1 kΩ, 2W resistor; 15 - electrolytic capacitor 40 μF, 450 V; 16 - ground; 17 - electrolytic capacitor 30 μF, 30V; 18 - 25Ω wirewound resistor; 19 - knife switch; 20 - rectifier; 21 - fuse; 22 - 100Ω, 25W vitrified resistor; 23 - 1.5 amp fuse; 24 - isolation transformer 220/220 V, 800 W.

A study of the spectra obtained in the visible, ultraviolet and extreme ultraviolet ranges, has shown that the described discharge in vacuum is a simple and convenient source of light. The spectra from a flash in vacuum between copper electrodes have a smaller background than those from a pulse in air; resonant lines of Cu I 3247 and Cu I 3274 do not show self-reversal, which is clearly visible in the spectra from a pulse in air. Also, the lines of Cu III and Cu II in the spectra from a vacuum flash are more intense than in spectra from a pulse in air.

Spectra of various substances in the vacuum range obtained by means of a DFS-6 spectrograph, have revealed lines of multiply-ionized atoms (C II–C IV, O II–O V, Ti II–Ti IV, Si II–Si IV, and others).

The experiments conducted show that a low voltage pulse discharge in vacuum can serve as a light source for various spectroscopic problems.

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On the Question of the Applicability of the Cowan and Dieke Function for a DC Arc

IU. A. SHERSTKOV

A definite model of a light source which must be used to solve a number of experimental problems [1,2], can be determined by prescribing the relative excitation function. From the physical viewpoint, the Cowan and Dieke model [3] is best for a dc arc and, consequently, it is interesting to confirm experimentally the applicability of this model to an actual light source.

By using two methods, the photoelectric and the photographic, we obtained intensity distributions in the plane of the central arc cross-section (see [1] for the combustion region) for the resonance lines of barium and strontium atoms and ions and also for the determination of the radial temperature behavior for the Cu I $\lambda = 5105$ Å and 5218 Å lines. The actual line intensity distributions along the arc radius were computed from experimental curves by the Hörmann method [4]. The temperature on the arc axis was 5600° K and diminished slowly reaching the value 3700° K at a distance $r = 3.6$ mm. Taking into account that $I_e(r) = n_e(r)$ const (where $n_e(r)$ is the density of radiating atoms, r is the distance from the arc axis along the observation path) and using the Boltzmann distribution, we calculated the function $\frac{n_a(r)}{n_a(0)}$ which defines the distribution of unexcited (absorbing) centers for the barium and strontium atoms and ions.

If the functions $\frac{n_e(r)}{n_e(0)}$ and $\frac{n_a(r)}{n_a(0)}$ are known, then it is not difficult to find the relative excitation function $E(y)$ [3] and also to determine exactly the absorption parameter p^* [3], at which self-reversal of the spectral line occurs.

In this case, finding p^* reduces to the graphical solution of the equation [3].

$$(1)\quad \int_0^2 E(y)\,(1-\mu y)e^{-\mu y}dy = 0,$$

where in our coordinate system

$$E(y) = \frac{\alpha}{2\beta}\ \frac{n_e(r)}{n_e(0)} \Big/ \frac{n_a(r)}{n_a(0)},$$

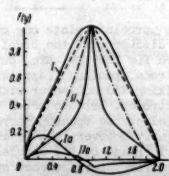
$$\alpha = \int_0^\infty \frac{n_a(r)}{n_a(0)}\,dr,\quad \beta = \int_0^\infty \frac{n_e(r)}{n_e(0)}\,dr.$$

and the r coordinate is related to y by means of the equation $y = \frac{1}{\alpha}\int_r^\infty \frac{n_a(r)}{n_a(0)}\,dr$.

The results of these solutions for the strontium atoms and ions are presented in the figure, where the lines $(1 - p^*y)$ and e^{-p^*y} are missing from this figure but the integrands of equation (1) for $\mu = p^*$ are superposed.

The calculated values of the parameters $\mu = p^*$ appeared to be equal for the lines BaII $\lambda = 4934$ Å, Sr II $\lambda = 4077$ Å, $p^* = 1.31$ and Sr I $\lambda = 4607$ Å, Ba I $\lambda = 5535$ Å, $p^* = 1.16$ and Ba II $\lambda = 4525$ Å, $p^* = 1.5$. The function $E(y)$ was calculated for the Ba II $\lambda = 4525$ Å, $p^* = 1.5$. The function $E(y)$ was calculated for the Ba II $\lambda = 4525$ Å line without relying on the function $T(r)$. Superposed on this same figure are the Cowan and Dieke functions

$$\left.\begin{aligned} E(y)/E(1) &= y^{n-1} \\ E(y)/E(1) &= (2-y)^{n-1} \end{aligned}\right\}\quad \begin{aligned} 0 &\leqslant y \leqslant 1 \\ 1 &\leqslant y \leqslant 2. \end{aligned}$$



Results of a graphical solution of the equation $\int_0^2 E(y)(1-\mu y)\,e^{-\mu y} = 0$

Ia - $E(y)(1-\mu y)e^{-\mu y}$ for $\mu = p^* = 1.31$; I - $E(y)$, experimental for barium ions ($\lambda = 4934$ Å) and strontium ions ($\lambda = 4077$ Å); IIa - $E(y)(1-\mu y)e^{-\mu y}$ for $\mu = p^* = 1.16$; II - $E(y)$, experimental, for barium ($\lambda = 5535$ Å) and strontium ($\lambda = 4607$ Å) atoms

The dashed curve corresponds to $n = 1.8$, the dot-dash curve to $n = 2.62$, where $p^* = 1.31$ and 1.16, respectively, for these functions are the solution of (1). This is explained by equation (1) having an infinite number of solutions for $E(y)$ for prescribed p^*, one of which characterizes the given light source. The difference in the functions $E(y)$, according to [3], is most influential on the dependence of $\frac{I_{max}}{I(0)}$ in the self-reversed line on

the absorption parameter

$$p = \frac{h\nu_0 BP(0)}{c} \frac{1}{2} \int_{-\infty}^{+\infty} n_a(r)\, dr,$$

where P(0) is the maximum value of the function determining the shape of the absorption line as measured in the units such that $\int_0^\infty P(\nu)\, d\nu = 1$.

We calculated this dependence by graphical integration for $p^* = 1.16$ and $p^* = 1.31$ by means of the corresponding experimental functions E(y) and the Cowan and Dieke functions. For $p^* = 1.16$, the difference between $\frac{I_{max}}{I(0)}$ at $p = 5$ reaches 20 - 25% and decreases sharply for $p^* = 1.31$.

According to Bartels computations [5], similar divergences are possible in the general case for large optical densities greater than 50%. We carried out such a computation within the scope of the Cowan and Dieke theory as applied to a dc arc. According to this computation, the greatest difference in $\frac{I_{max}}{I(0)}$ is ~20% only for $p^* < 1.26$ ($n > 2$) and is less than 5% for $p^* > 1.26$. This does not contradict Bartels conclusions but is a particular case for a dc arc which burns freely in an air atmosphere.

From this, it follows that the Cowan and Dieke function can be used to compute the line shape emitted by a dc arc. The exceptions are resonance lines of atoms with low ionization potentials, where the errors can reach 20%.

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A Simplified Method for Spectral Analysis of Inert Gases for Impurities

O. P. BOCHKOVA, L. P. RAZUMOVSKAIA, S.E. FRISH, AND N. V. CHERNYSHEVA

The rapid growth of industrial production and the use of large quantities of inert gases of a high degree of purity create new demands for methods controlling the purity of gases. The majority of existing methods for analyzing the impurities in inert gases are not used in industry, some because of insufficient accuracy and sensitivity [1], others because of the relatively long time [2] required for carrying out the analysis.

The simplified method which we have worked out for the spectral analysis of argon for nitrogen content [3] permits control of the purity of argon to be carried out successfully right in industry.

The method does not require complicated apparatus. A spectral instrument is replaced by a filter which isolates the required region of the spectrum. A discharge is excited in a capillary by a high frequency generator.

The gas to be analyzed is drawn continuously through the capillary by a fore-vacuum pump. Radiation proportional to the concentration of the impurity is registered by an FEU-19 photomultiplier connected to an indicating microammeter. The sensitivity of the method is 0.001%, the accuracy ~10%.

We also used this simplified method of analysis to detect impurities of hydrogen in helium, neon in helium and a neon-helium mixture in nitrogen. The table gives the range of the concentration of the impurity being studied, the filter used to isolate the spectral region of the impurity, the radiation detector, and the conditions for excitation of the spectrum of the gas mixture.

Detection of hydrogen in helium, neon in helium and a neon-helium mixture in nitrogen was carried out without circulation, in a closed discharge tube. This was necessitated by the lack of the large amounts of gas which permit use of a circulation system. The calibration curves for detection of H_2 and Ne in He, and He-Ne in N_2 are shown in Figure 1.

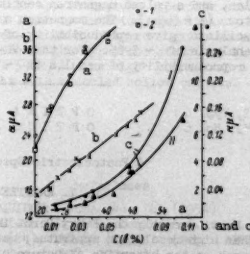

Figure 1. Calibration Curves.

a) Ne-He in N_2 (1. 10% He, 2. Without He); b) Ne in He; c) H_2 in He (I. I_{red}/I_{yellow}, II. $I_{blue\text{-}green}/I_{yellow}$).

The methods of spectral analysis of gases are not unstandardized; when they are used in industry the question of standardization is essential. In detecting nitrogen in argon the instrument was calibrated directly in concentration according to previously prepared standard mixtures. Periodic verification of the calibration of the instrument can be made against one standard which may be selected from the finished product and stored under high pressure (~150 atm.).

In order to detect neon in helium we recommend making calibrated discharge tubes with standard mixtures. We tested the possibility of making such standardizations on mixtures of 0.2% Ne, 1.2% Ne, and 5% Ne in He. Tubes were made in the form of a 1 mm. capillary attached to a 200 cm^3 bulb (Fig.2). The distance between the external annular electrodes was rigidly fixed and equaled 1.5 cm. The pressure of the mixture was 40 mm. Hg.

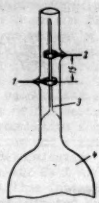

Figure 2. Tube for a Standard Mixture.

1, 2, External electrodes with leads. 3, Capillary (diameter 0.5 mm). 4, Bulb (volume 200 cm^3).

The constant proportions of Ne-He were checked for 10 months. Measurements of the ratio of Ne and He line intensities were made both photographically on an ISP-51 spectrograph and photoelectrically with filters.

The discharge was excited by generators of various types: a VG-2 generator, a low-power GU-29 vacuum tube oscillator at a frequency of 30 megacycles, and a pulsed magnetron centimeter wave oscillator (λ = 3 cm). The magnetron and the low-power oscillator give reproducibility of the results of the analysis of ~ 5-6%. For the VG-2 generator the reproducibility of results is ~ 10-15%.

It has been established that the relative intensity of He-Ne lines in spectra of standards of this type does not change with time within the limits of error of measurement, and these standards may be used to plot calibration curves for no less than six months.

Conditions for Analysis of Inert Gases for Impurities

Gas Mixture under Analysis	Range of Concentration of the Impurity (in %)	Conditions for Excitation of the Gas Mixture	Radiation Detector	Light Filter
Nitrogen in Argon	0.001-0.01 0.01-0.1 0.1-1 1-20	Diam.1 mm p-50-100 mm Hg., p-2-5 mm Hg.	FEU-19 STsV-3	UFS-3 UFS-4 λm 366 mμ
Hydrogen in Helium	0.01-1 and higher	Diam.2 mm p-5-10 mm Hg.	FEU-17 FEU-19	λm 656 mμ λm 588 mμ λm 486 mμ
Neon in Helium	0.001-1 and higher	Diam. 0.5 mm p-80 mm Hg.	FEU-19 FEU-22 with dc amplif.	Red glass λm 630 mμ
Neon-Helium Mixture	20-35 5-10	Diam.0.5 mm p-2 mm Hg.	FEU-19 FEU-22 with dc amplif.	λm 630 mμ λm 588 mμ Monochromator λ 4471 Å

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A Photoelectric Spectrometer with a Fabry-Perot Interferometer

N. I. KALITEEVSKII, G. M. MALYSHEV, AND M. P. CHAIKA

Until recently the Fabry-Perot interferometer, like other high resolution apparatus, was used only in research on the hyperfine structure of spectral lines and very narrow multiplets of fine structure. At present, improvements in experimental technique (primarily due to the use of dielectric reflecting films which absorb very little light) have made it possible to use a spectrometer with a Fabry-Perot interferometer for solution of a much wider range of problems. This relates to determination of the position and relative intensity of Raman components, study of absorption spectra, various astrophysical applications, carrying out isotopic spectral analysis, etc. A special prospect is use of the spectrometer in the infrared spectrum.

The research of Jacquinot [1], Chabbal [2], and Chaika [3] has shown that, when the parameters of the apparatus are properly selected, the luminosity of such a spectrometer is much greater than the luminosity of a spectrometer with a diffraction grating, not to mention the luminosity of a prism spectrometer.

This article will consider the parameters of the photoelectric apparatus built in the NIFI LGU.

The optical arrangement of the apparatus, shown in Fig. 1, was selected in accordance with the assertion made earlier [4] that at a given resolving power the greatest luminosity of the apparatus is obtained by isolating the central part of the interference ring while scanning by varying the optical path difference by some means or other.

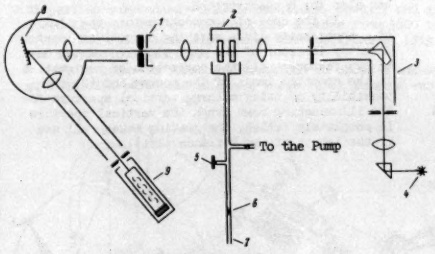

Figure 1. Optical arrangement of a spectrometer with a Fabry-Perot interferometer

1. Circular diaphragm;
2. Interferometer in a chamber;
3. Preliminary monochromator;
4. Light source;
5. Safety valve;
6. Capillary;
7. To the high pressure bulb;
8. Diffraction grating;
9. Photomultiplier.

The Fabry-Perot interferometer with dielectric reflecting layers provides the high resolving power of the apparatus. The seven-layer film (TiO_2 and SiO_2) for this interferometer was obtained by a chemical process in the laboratory of T.N. Krylova [5]. The interferometer was placed in an airtight chamber, in which the pressure could be varied from a few mm. Hg. to atmospheric. Scanning uniformity was assured by feeding the gas (nitrogen) from the cylinder under high pressure (~100 atm.) through the narrow capillary 6. A ring of constant inclination was focused by an N-11 lens onto the plane of the slit of a diffraction monochromator. Here there was a circular diaphragm which cut out a given part of the central interference ring. A 300 line per mm grating with a groove profile giving a blaze angle of 31° was used in the monochromator. The work was done in the seventh order of the diffraction spectrum for the green region and in the fifth order for the red region. The large angular dispersion of the instrument permitted work with sufficiently wide slits to assure high luminosity of the apparatus.

To avoid overlapping of the orders of the diffraction spectrum, a preliminary monochromator with a constant deviation prism was used. Such preliminary monochromatization permitted detection, by the simplest means, of the required part of the spectrum in cases where loss of light equaled that lost in filters (less than 50%). The preliminary monochromator also acted as an intermediate slit. This also got rid of the false images of the system of interference rings which exists when using extended sources of light. The geometric parameters of the apparatus were selected in accordance with calculations of the system carried out earlier [3].

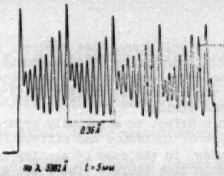

Figure 2. Trace of the hyperfine structure line of holmium λ5982 Å. Distance between reflecting layers of the interferometer d=5 mm.

The light signal was received by a photomultiplier, and the photocurrent through the DC amplifier was registered by an automatic potentiometer EPP-09. As a result of comparison of the various types of photomultipliers, the following were selected: for the blue and green regions of the spectrum, the FEU-17 multiplier, for the yellow and red regions, the FEU-12 and FEU-14 (bismuth photocathode), and an FEU-22 for registering emission above 6600 Å.

When registering small light currents, in order to decrease fluctuation of the dark current, the time constant of the amplifier was increased (R = 100 M, C = 0.25 μf), and the scanning speed correspondingly decreased. The circumstances of the work [6] were considered when calculating the admissible speed, although the shape of the curve in our case differed somewhat from the Gaussian. For a scanning speed of 0.0045 cm/sec. (interferometer d=30 mm), the decrease in peak intensity was ~4%, the line broadening ~4%. Experiments conducted at various scanning speeds confirmed the applicability of such calculations in the given case.

On this apparatus, the hyperfine structure of isotope lines of lutetium, gadolinium, and holmium were studied. Figure 2 gives an example of the trace of the hyperfine structure line of holmium λ 5982 Å. The light source was a discharge tube with a cooled hollow cathode.

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Concerning Some Possible Improvements of Vertical Astigmatism Instruments Using The Rowland Circle. Vacuum Monochromator With A Concave Grating And A Toroidal Mirror

IU. P. SHCHEPETKIN

It is well known that vertical astigmatism is the basic shortcoming of instruments in which a grating, an entrance slit and a cassette (in the case of a monochromator--an exit slit) are mounted on a Rowland circle.

This defect is especially pronounced at large angles of incidence and diffraction, in in particular, in the case of grazing incidence in in the vacuum ultraviolet. The spectral images of a point source are vertically elongated thin astigmatic lines on the cylindrical surface obtained by moving the genetrix along the Rowland circle. Vertical astigmatism greatly reduces the brightness of the spectra and thus reduces the effectiveness of the grating in solving many problems in spectroscopy.

Methods of increasing the brightness of spectra by increasing the size of the source or the length of the entrance slit, or by placing cylindrical lenses in front of the spectrum to focus the spectral lines lengthwise (in essence, compensating the astigmatic difference), are not always usable.

Although gratings which are toroidal [1] and aspherical to one plane of symmetry [2], [3], also make it possible to correct vertical astigmatism, technological difficulties have so far prevented their manufacture. The search for simple and practical solutions to this problem is of considerable interest.

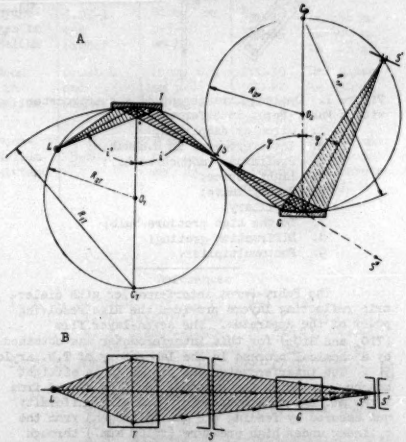
The proposed method of compensating for the astigmatism introduced by a concave grating employs a spherical, or better, a toroidal mirror T (see diagram) opposite the entrance slit. This mirror also acts as a condenser. In the proposed method of illumination, source L, toroidal mirror T, and entrance slit S of the monochromator are located on a circle with center O_1, and radius R_{2T}, equal to half the radius of curvature R_{1T} of the meridian section of the toroidal mirror (C_T is the center of curvature of the mirror). In such an arrangement, the meridian rays of toroidal mirror T image source L on the entrance slit S of the monochromator at unit magnification. Grating G in turn gives a spectral image S' with a meridian magnification equal to unity.

Rays in a sagittal section of the beam (see figure B) image the source in the proximate sagittal focus S" of the grating. This point is obtained by calculating the reverse path of an astigmatic beam coming from a spectral point S'on the Rowland circle of radius R_{2p} with center at O_2. C_p is the center of curvature of the grating, R_{1p} is its radius of curvature. The sytem as a whole gives spectral image of the source free of astigmatism.

With a constant angle of incidence and a variable angle of diffraction (changing $k\lambda$) as before, it is possible to compensate for astigmatism: for this it is necessary only to move the source and toroidal mirror to appropriate new positions.

In spectra on both sides of the stigmatic point, astigmatism increases slowly. This design may therefore be used not only for a monochromator, but also for a spectrograph.

In the case of a monochromator, the flux of monochromatic light striking a receiver located directly in front of the exit slit, increases due to two factors: (1) the correction of astigmatism in the spectral image of the source and (2) the possibility of using a large vertical aperture for the illuminating beam (when the vertical aperture is completely filled, the grating makes full use of the length of the entrance slit).



A - Schematic of monochromator with concave grating and toroidal mirror (upper view);
B - the same (front view).

The effectiveness of the monochromator is especially high with a small source and for work in the vacuum ultraviolet(grazing incidence); on receivers of limited dimensions, the flux of monochromatic light may be increased by ten or more times compared to common monochromators without toroidal mirrors using the same source placed directly before the entrance slit.

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DFS-12 High Intensity Spectrometer with Diffraction Gratings

S. L. BERKOVICH, M. V. GOFREN, M. V. LOBACHEV,
T. K. FAL'K and D. I. SHARONOV

In 1957 the collective of the factory designed and built a new high luminosity spectrometer, DFS-12, with diffraction gratings and photoelectric registration of spectra.

The spectrometer permits reception of Raman spectra not only for transparent fluids, but for diffuse-dispersion substances - cloudy solutions, powders and glass, the study of which was particularly difficult up until now. The spectrometer has a range from 3600 to 6400 A.

The optical arrangement of the spectrometer (Fig. 1) shows the double mirror monochromator with two diffraction gratings.

In order to correct aberrations we chose a non-symmetrical arrangement of light incidence on a grating with parabolic mirrors, whose focal lengths were 800 mm and relative aperture, 1:5.3.

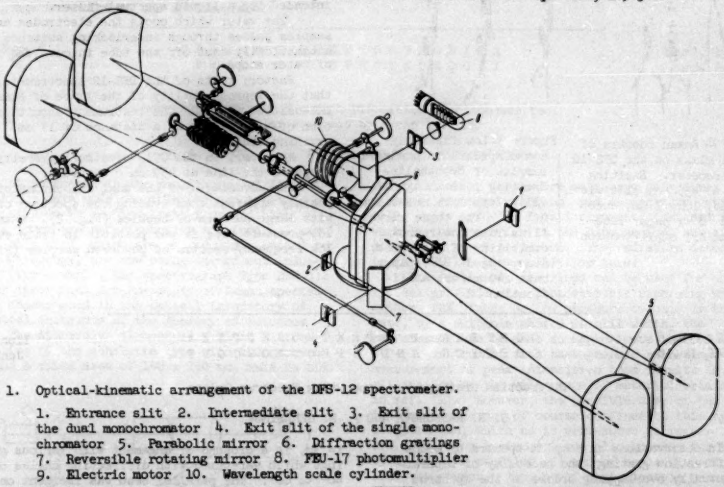

Figure 1. Optical-kinematic arrangement of the DFS-12 spectrometer.

1. Entrance slit 2. Intermediate slit 3. Exit slit of the dual monochromator 4. Exit slit of the single monochromator 5. Parabolic mirror 6. Diffraction gratings 7. Reversible rotating mirror 8. FEU-17 photomultiplier 9. Electric motor 10. Wavelength scale cylinder.

The gratings have 600 lines mm, a ruled section 140 x 150 mm, and operate in the second order, concentrating 60% of the light in the region of the spectrum from 4300 to 4700 Å. They were mounted on one table on the principle of combined gratings proposed by Kiselev. The dispersion of the dual monochromator is 5 Å/mm.

Symmetrical curved slits 40 mm high were used in the instrument. The slits open to 2.2 mm. The accuracy of reading of the width of the slit in the interval to 0.2 mm is 0.001, in the remaining interval, 0.01 mm.

The intermediate exit slit and the reversible rotating mirror permit use of the instrument as a single monochromator with 10 Å/mm dispersion.

The table with the diffraction gratings is turned by a synchronous electric motor with constant angular speed. The speed of the passage of the spectrum over the exit slit may take eight fixed values within the wide range 0.25 to 25 Å/min.

The scale of the instrument is numbered in angstroms. The evenness of rotation of the gratings is assured up to 2 , which corresponds to 0.5 Å on the scale.

The instrument permits registration of spectra in both directions. For ease in deciphering, a special marking device marks reference lines on the trace every 40 Å. Connected with the wavelength scale are adjustable terminal switches which permit stopping the instrument automatically at any point in the working range.

The light energy receptor is an FEU-17 photomultiplier which is set in a hermetically sealed enclosure and can be placed behind any of the exit slits of the monochromator. The signal from the photo-multiplier goes into a DC amplifier with 100% feedback, which permits using, as a final stage, a small electronic self-recording PSI-02 potentiometer with a 10 mv scale and a time constant of 2 sec. The sensitivity of the whole arrangement assures the tracing of spectral lines with an energy of 10^{-13} watts. Within the limits of error of measurement, which depends on the reproducibility of the trace, the system is linear.

Along with the spectrometer, an illuminator for excitation of Raman spectra was designed and built. A special feature of the illuminator is the use of spiral mercury low pressure tubes with water-cooled electrodes. In the spectrum of such tubes, the continuum is almost completely absent, and the width of the spectral lines does not exceed several hundredths of an angstrom. The tube is operated on regulated direct current of 6-12 amps from a rectifier.

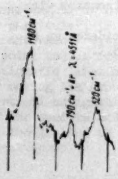

Figure 2. Raman spectra of No-31 glass on the DFS-12 spectrometer. Exciting line $\lambda = 4358$ Å; slit width 2.2 mm, 1mm, 1 mm; sweep speed "8" ; paper rate 720 mm/hr; amplification "5".

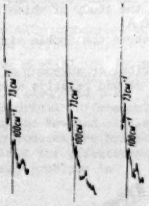

Figure 3. Low frequency Raman spectra of powdered samples of Naphthaline. Exciting line $\lambda = 4358$ Å; slit width 0.25 mm, 0.1 mm, 0.1 mm. The three curves illustrate the reproducibility of the trace; Sweep speed "6" ; paper rate 240 mm/hr; amplification "2".

The illuminating system is changeable and permits filling the whole aperture of the instrument with samples of three different diameters. In the case of small diameters, prism image dividers cut the light beam into three verticle bands and dispose the latter one after the other lengthwise on the slit of the instrument, illuminating the whole height of the slit.

For liquid samples, cells of internal diameter 9.13 and 18 mm, 80-100 mm long in the working part, are included in the assembly of the illuminator.

Between the body of the tube and the sample under study is a cylindrical section with two cavities. Cooling water circulates through the external cavity, while the internal cavity is intended for a liquid spectral filter.

The water which cools the electrodes and the samples passes through interlocking switches which automatically shut off the tube in case the flow of water stops.

Factory tests of the DFS-12 spectrometer showed that the reproducibility of the trace of Raman spectra intensities is 2%. The instrument permits resolution of a weak line at a distance of 11 cm^{-1} from the exciting line.

Moreover, in the CCl_4 spectrum asymmetry of the shape of the line at 459 cm^{-1} was seen.

The advantages of the dual monochromator are plainly apparent when tracing the spectrum of glass with large numbers of bubbles (Fig. 2). Thanks to the low-pressure tube it was possible to trace even the low frequency spectra of powdered samples (Fig. 3).

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Diffraction Gratings For Separating Spectrum Orders

G. N. RASSUDOVA AND F. M. GERASIMOV

In observations on complex spectra by means of diffraction gratings the necessity of separating mutually overlapping orders of the spectrum often arises. In some cases, as for example in working with precision echelles, one can accomplish this by using an auxiliary dispersing system of low dispersion, the direction of the dispersion being perpendicular to that of the principal system.

The resulting spectrogram forms a two-dimensional array. Prisms [1, 2] as well as ordinary diffraction gratings [3,4] have been used as the dispersing element of the auxiliary system. Because of their high dispersion the latter can be employed only in combination with gratings with a groove spacing of 100 μ or greater.

We have prepared reflection gratings of a special type, which can be used as order separators for gratings with any groove spacing. These separator gratings have 50 or 100 grooves per mm. The grooves are in the form of steps with the working faces inclined to the surface of the grating by an angle of about 1° ; in this way one obtains a high concentration of light in the first order, which is the working order.

Testing of the separator gratings was carried out with an autocollimating spectrograph, f= 3m, in a crossed arrangement with various gratings which were used with diffracting angles of 40° to 60°. The parallel beam was incident on the separator grating at an angle of 20° to 45° in the plane parallel to the grooves which were placed horizontally. After diffraction from the principal grating, placed with its grooves vertically, the beam was incident a second time on the separator grating and then passed into the objective.

With this relative disposition of the gratings multiple diffraction of the beams between them is eliminated; at the same time, however, weak subsidiary lines coming from neighboring orders of the separator grating appear in the spectrum. These subsidiary lines are tilted and therefore easy to recognize. The relative intensities of the subsidiary lines depend on the distance between the gratings and on the distribution of the intensity in the spectrum of the separator grating. In the region of maximum light concentration the intensity of the subsidiary lines is insignificant, but increases rapidly as the distance from the maximum increases. Owing to the presence of such lines and to the superposition of the spectral orders of the separator grating, it is possible only to photo-

graph simultaneously regions of the spectrum within the limits of half an order in both the visible and the ultraviolet regions. The distance between cycles (orders) on the spectrogram increases with increasing wavelength.

If a separator grating with a constant of 20μ is used in the arrangement described and if the principal grating has the same constant and a diffraction angle of about 40°, a photographic plate measuring 9 x 12 cm is able to contain a region of the spectrum somewhat greater than 2000 Å in an array of approximately 25 cycles. The overall length of the spectrum amounts to about 2 m. The dispersions in the regions 3000 Å and 4500 Å are 0.6 and 0.9 Å/mm, respectively.

The original separator gratings can be replaced by replicas without any loss in the quality of the image formation of the spectrograph.

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Some Applications of a High-Dispersion Spectrometer to Molecular Analysis by Raman Spectra

V. A. ZUBOV, G. G. PETRASH AND M. M. SUSHCHINSKII

Recent successes in the manufacture of diffraction gratings have made possible the construction of spectrographs in which high light flux and high resolving power are satisfactorily combined. Instruments of this kind, which are particularly suited to Raman spectroscopy, are now being turned out industrially (for example, the spectrograph Type DFS-4). A similar instrument for the study of Raman spectra has been constructed in the Optical Laboratory of the Physical Institute of the Academy of Sciences (FIAN). The dispersive element is a plane diffraction grating of the echelette type with 600 grooves per mm and a ruled area of 140 x 150 mm, made in GOI.

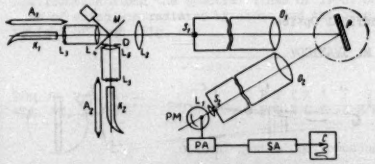

Figure 1. Optical Arrangement for the Difference Method.

P - diffraction grating; O_1 and O_2 - objectives; S_1 and S_2 - slits; L_1 - lens; A_1 and A_2 - radiation sources; K_1 and K_2 - Raman tubes; L_3, L_4 and L_5, L_6 - telescope systems to give intermediate images of the Raman tubes; D - diaphragm for regulating the intensity of the "subtracted" beam; M - modulator (rotating mirror with segments cut out, allowing first one and then the other beam to fall on the entrance slit); L_2 - condenser; PM - photomultiplier; PA - preamplifier; SA - selective amplifier; C - recorder.

The collimating lenses are telescope objectives with a focal length of 1600 mm and an aperture ratio 1:12, made by GOI. This instrument, designed for work in the 2nd order in the blue region, has a dispersion of 5 Å per mm. The radiation detector is an FEU-17 photomultiplier tube.

The instrument described can be used for analytical problems with photoelectric recording using either PRK tubes or low pressure tubes. In this case, by a suitable choice of slit width, the performance can be made to approximate that of an ISP-51 instrument with photographic recording. The measurement of peak intensities then permits the utilization of the wide range of material obtained in ref. [1]. However, the possible uses of the instrument are not of course confined to this type of operation, which as is well-known is rather ordinary. The instrument can also be used for the study of line profiles [2] and of bands with close line structures. The use of photoelectric recording increases the accuracy and simplifies the reduction of results; the possibilities of the use of the spectrometer for molecular analysis are thus widened. Other possibilities are also evident.

The first of these is the use of the double beam method. In this method the ratio of two light signals is recorded, one coming from the tube containing the scattering substance and the other taken directly from the lamp furnishing the exciting radiation. Thus one can eliminate the effect of intensity fluctuations in the exciting source and of instability in the operation of the photomultiplier and the amplifier circuit. We have used a method of optical scaling similar to the system used in the double-beam infrared spectrometer AIKS FIAN-4 [3]. This arrangement is described in detail elsewhere [4].

A second possibility is the use of the difference method. The optical diagram for this case is given in Fig. 1. Light is directed onto the entrance slit of the spectrograph alternately from two different sources by means of a rotating mirror.

When the two light beams are equal in intensity the resulting photocurrent in the multiplier tube is unmodulated and is not passed by the selective amplifier which is tuned to the modulation frequency. When one light beam has a higher intensity, the resulting photocurrent contains an alternating component which is amplified and activates the recorder. In this way the difference of the two signals is recorded. Similar methods are widely used in infrared spectroscopy (cf. for example, ref. [5]). In Raman spectroscopy the method has not yet been used so far as we are aware.

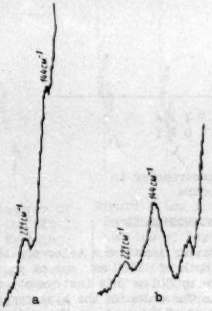

Figure 2. (a) Spectrum of 1-methyl-2-ethyl benzene with the slits chosen to produce extensive overlapping of the lines; (b) Difference spectrum of 1-methyl-2-ethylbenzene with the Rayleigh line of benzene "subtracted".

The following possible uses of the difference method in Raman investigations might be indicated. 1) Elimination of background interference in the region close to the exciting line. In this case the Rayleigh line of a substance with a structure similar to that of the scattering substance is "subtracted" from the Raman spectrum of the latter (Fig.2). This permits, for example, the study of low frequency lines, which are difficult to investigate by other methods. 2) The investigation of mixtures in which lines of interest in analytical work are covered up by lines of another component of the mixture. Here, the spectrum of the interfering component with matching intensity is "subtracted" from the spectrum of the mixture. 3) The study of small changes in the width and in the intensity of lines in the investigation of solvent influence and temperature effects.

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Raster Illuminators with Cylindrical Optics

A. K. VINOGRADOVA AND L. M. IVANTSOV

One of the basic sources of error in spectral analysis is uncontrolled selective loss of radiation in the path from the radiating extended source to the plane of the spectrum. Selection of the optical arrangement of the illuminator and its parameters has a decided relation to this effect. In the effort to control the selective loss of radiation, and also in certain other regards, the best prospect seems to us to be raster illuminators with cylindrical optics. The purpose of the present article is to analyze the operation of a cylindrical raster illuminator as an element in a spectral apparatus, and also to acquaint the reader with the results of a study of such illuminators. Raster systems with cylindrical optics and mirror raster systems in particular are only referred to in the literature. In our experience, their production and assembly is considerably simpler than the production and assembly of rasters with spherical optics [1,2].

Let us analyze in more detail the operation of rasters with cylindrical optics. When there is no raster, the light source fills the collimator lens only along the vertical diameter (Fig. 1, a).

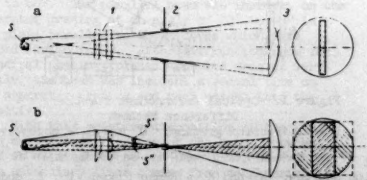

Figure 1. Collimator lens with a raster illuminator with cylindrical optics filled along the vertical (a) and horizontal (b) diameters.

1 - raster 2 - entrance slit 3- collimator objective

Insertion of a raster between the source and the slit has no effect on filling the lens vertically or on the uniformity of illumination of the slit. The raster substantially changes the filling of the collimator and the slit illumination in the

horizontal section. Each of the quasi-sources S', S'', ..., S^n fills its own zone in the horizontal section. If necessary the focusing properties and dimensions of the lenses can be calculated so that the lens can be fully used along the horizontal diameter as well (Fig. 1, b).

Each source point is diffused at the plane of the slit into a rectangular band whose width is determined by the rays passed by the outer lenses of the raster through the given source point and its image. The center of the horizontal section of the spot is always illuminated by all the points while the edge is only illuminated by the outer points of the horizontal section of the extended source. Even when the collimator is not completely filled, not only the center but the spot zone adjoining it on the slit are filled with light from all points of the horizontal section of the extended source. Therefore, generally speaking, a shift in the discharge in the horizontal plane may be the reason for a change in the spectral composition of the light entering the spectral apparatus. Depending upon the distance of the source from the slit, the light beam in the plane of the collimator will remain practically stationary even for marked shifts of the source either to the side or upward. Therefore, selective loss of radiation on the collimator caused by shifting the source does not occur in practice even when the effective aperture of the collimator is filled.

Calculation and experiment show that when the horizontal section of the collimator is filled, the raster condenser is less sensitive to horizontal, and even more to vertical, shifts of the source in comparison to a three-lens condenser. Shifting the source in the vertical plane is permissible within limits determined primarily by the conditions of selective light vignetting by the electrodes.

The advantages of the raster illuminator with cylindrical optics over the three-lens illuminator are well illustrated by a graph of the blackening distribution along the spectral lines of iron, one line of which was radiated by atoms and the other by ions of iron (Fig. 2).

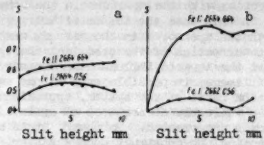

Figure 2. Blackening distribution along the spark and arc lines of iron when using a raster illuminator with cylindrical optics (a) and a three-lens illuminator (b).

It must be mentioned, however, that in principle raster illuminators with cylindrical optics are less luminous than the three-lens illuminator since they focus light only in the horizontal section.

However, when working with sources such as an arc or a spark, the real loss in luminosity, if it exists, is very insignificant.

It must be precisely specified what filling the collimator with light from the arc or spark means. Ordinarily we speak of filling a collimator with radiation from an extended source as a whole, forgetting its zonal structure. It is perfectly evident that under certain conditions the collimator is filled quite differently in the light of lines of various kinds. Consequently the resolution of the spectral apparatus will vary also. Use of the raster illuminator permits reducing this effect to a minimum since each source point is imaged on the plane of the collimator lens by broad rays approximately equal to the aperture in both sections.

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TOM VI, Vyp. 6 OPTIKA I SPEKTROSKOPIIA Iiun', 1959
VOL. VI, No. 6 OPTICS AND SPECTROSCOPY June, 1959

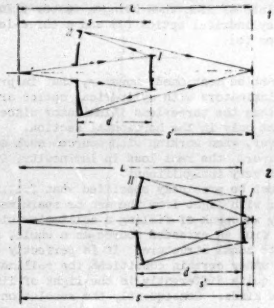
Optical System for Focusing Infrared Radiation on Small Receivers

I. V. PEISAKHSON

In many spectral devices for the infrared region (for example IKS-11, IKS-6) the radiation which is passed through the exit slit of the monochromator is focussed on the receiver with the help of an elliptical mirror. Along with the difficulties of obtaining an ellipsoidal surface of high quality, it is necessary at the same time to impose rigid limitations on the dimensions of the receiver structure, which will have to accommodate the bundles of rays which are falling on the mirror. In addition, the image of the exit slit on the receiver, which is free from aberrations at points on the axis of the mirror, has significant coma on the off-axis points.

Free from the mentioned deficiencies are projecting systems which consist of two spherical mirrors, one convex I and one concave II. These are a system with an aperture in a concave mirror (sketch 1 - see figure), first applied, apparently, in 1950, as an infrared microspectrometer objective (Gershgorin's calculation) and a system with an aperture in both mirrors (sketch 2), suggested as an inverting mirror micro-objective as far back as 1951 by V. M. Chulanovskii for imaging the exit slit of a monochromator on the surface of a thermal receiver. The second system was manufactured by the Experimental Workshop of the Physical Institute LGU (author's design) for the infrared spectrometer ISP-1. A particular case of the second system was described by Greenler [1] in 1956 (the slit coincides with the aperture in the concave mirror, its

image coincides with the aperture in the convex mirror). In this case the losses of energy, connected with the apertures in the mirrors were minimized, but correction of the spherical aberrations, which exert the largest influence on the spreading of the slit image, is possible only at one value of the reduction ratio of the system, approximately equal to 4, while the aberrations of an inclined bundle remain uncorrected. Moreover, it is not always practical to construct such a system.



We made an investigation of the aberrations of both two-mirror systems with different reciprocal arrangements of the slits, mirrors and receivers for reduction ratios of 4 to 10 and compared them with the aberrations of an elliptical mirror with the same reduction. It turned out that one may correct the spherical aberrations with both systems at a given reduction, while one of the parameters of the system (the distance d between the mirrors or the distance S from the slit to the first concave mirror) remains fixed. Therefore in sketch 1, by a suitable choice of construction of the elements, one may correct for coma. In sketch 2 coma may not be eliminated.

Trigonometric calculations showed that with identical transverse dimensions, scheme 2 may be considered equivalent to an elliptical mirror in quality of the mirror, but scheme 1 gives qualitatively a considerably better image at not too large apertures (approximately up to 0.5 the space of the image). With corrected spherical aberrations, the first scheme is shorter than the second. The loss of energy in scheme 1 in connection with the shielding of a bundle of light by the first (convex) mirror is slightly less than in scheme 2, where it is determined by the size of the aperture in the convex mirror. In both cases, with 4-10 reductions of the systems and with spherical aberrations corrected, the shielding of light which arises from points on the axis of the system does not depend in practice on the reduction and constitutes no more than 15-20% (by area).

If the remaining aberrations of all three projection systems with a given slit height and reduction are compared with an identical one of length L then both two-mirror systems give a better image than an elliptical mirror.

In order to avoid vignetting of the inclined bundles and to reduce the dimensions of the mirrors and apertures in them with a high monochromator slit it is expedient to place nearby a collector, designed for the first scheme so that the entrance pupil is on the convex mirror, and for the second, so that the exit pupil would be the aperture in this mirror. A simple lens of any material, transparent in the region of the spectrum to be investigated, (for example, fluorite, rock salt, potassium bromide) may serve as a collector. Introduction of the collectors, with spherical aberrations corrected, does not change the amount of other aberrations.

The advantages of two mirror projection systems are simplicity of manufacture, compactness, the possibility of choosing parameters depending on the requirements, imposed on the structural shaping of the system. These give reason to think that such schemes may replace the expensive elliptical mirrors in those spectral devices, where sharp imaging of the exit slit on the radiation receiver is required.

Reference

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TOM VI, Vyp. 6 OPTIKA I SPEKTROSKOPIIA Iiun' , 1959
VOL. VI, No. 6 OPTICS AND SPECTROSCOPY June , 1959

Microscope-spectrophotometers

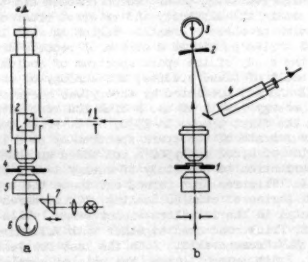
L. S. AGROSKIN AND N. V. KOROLEV

The combination of a spectrophotometer with a microscope allows the extension of well-developed methods of absorption and fluorescence analysis to the study of small objects and small areas of larger objects. Because of the complexity of the optical design of the microscope giving the image, a simple combination of these devices does not provide optimum photometric conditions. For this reason the development of special apparatus is demanded, taking into consideration the peculiar nature of such types of analysis.

We propose two principal microscope-spectrophotometer arrangements which are distinguished optically by the relation between the observation and the measuring system.

The first is the luminous probe scheme (figure a.) Here the exit slit of a monochromator is replaced by a very small aperture 1. This aperture is projected onto the surface of the preparation 4 by aid of the half-aluminized cubical prism 2 and the microscope objective 3. The light focused by the objective on the point of the preparation under investigation

next passes through the condenser 5 to the receptor 6. For visual observation and location of the preparation in the photometric field, the microscope and supplementary illuminating scheme including the prism 7 is employed. The method of locally illuminating the object at the moment of measurement significantly reduces the volume of scattered light and in all probability decreases its harmful effect.



In equipment constructed on the principle of the luminous probe for the measurement of optical density of microscopic objects, the probe dimension is about one square micron for the visible and ultra-violet emission lines of the mercury spectrum. In work with the hydrogen lamp the size of the luminous probe is no smaller than 100 square microns.

The second scheme (figure b) proposes the projection by the microscope objective of the image in monochromatic radiation onto the opaque screen 2, represented as a concave mirror with a central aperture. Radiation passing through this aperture, i. e. through the conjugate point of the preparation 1, falls on the photomultiplier tube 3. For visual observation the optical system 4 is used to focus on the mirror. The arrangement allows the conduction of uninterrupted observation of the object during the process of measurement. There are different feasible variations of this scheme, among them photometric measurements with any microscope.

The first and second principal schemes may be combined, as is done in an experimental model manufactured as the MUF-4 ultraviolet microscope-spectrophotometer.

The complexity of the form of microscope objectives, which in general distinguishes them from plane-parallel plates, and in addition the specific requirements of the measuring scheme stipulate a lower sensitivity to concentration and a lower accuracy of micro- in comparison with macro-absorption measurements. The magnitude of the errors, however, depends on the concrete circumstances and may be adequately allowed for.

In concluding we shall enumerate those aspects of spectroscopic work which were successfully realized in the above described equipment.

1) The determination of the absorption spectrum in the visible and ultraviolet regions: a) biological specimens, among them details of individual cells, b) stained sections, c) coacervated drops, d) solutions in microvessels e) organic and inorganic microcrystals.

2) Determination of fluorescence spectra: a) organic microcrystals, b) living algae.

3) Direct determination of the ultraviolet absorption spectra of the spot in paper chromatography.

4) Determination of the reflection spectra in metals and minerals.

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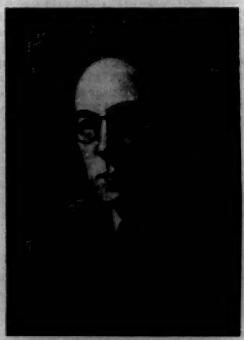
ANNIVERSARIES AND DATES

SERGEI EDUARDOVICH FRISH

(On his 60th Birthday)

June 19, 1959, marked the 60th birthday of Professor Sergei Eduardovich Frish, one of the most prominent Soviet spectroscopists and corresponding member of the Academy of Sciences of the USSR. The long-term scientific and pedagogic activity of S. E. Frish is characterized by a wide range of interests, skill and also as by firm insistence on purity and exactness in experiments. He is known as a student and one of the closest associates of academician D. S. Rozhdestvenskii, the founder of Soviet optical science. In 1918, while a 2nd term student, S. E. Frish enrolled as a laboratory technician at the Government Optical Institute and combined study in his chosen field with mastery of technology of experiments. After graduating from the University in 1921, S. E. Frish worked at the Government Optical Institute and taught at the University. From 1939 on, all his activity has centered on the University of Leningrad, where he held the professorship in optics on a permanent basis and where, in the course of twenty years (1937 to 1957), as dean and later as director of the Institue of Physics, he supervised the scientific and educational work of the Faculty of Physics. In 1934, S. E. Frish was given the title of full professor and in 1946 he was elected as a corresponding member of the Academy of Sciences of the USSR.



In the early years, the educational activity of S. E. Frish was basically devoted to the development of two extremely essential trends in spectroscopy - the systematism of atomic spectra and the study of the hyperfine structure of spectral lines.

As early as 1922, at the 3rd Congress of the Russian Association of Physicists, he reported on fine experiments regarding the magnetic splitting of the line of sodium and potassium. In 1925, he discovered new Zeeman components of several lines of these elements, the position of which corresponded well with the theory of Sommerfeld. In 1929, he thoroughly studied the lines of the diffuse series of sodium and potassium with the aid of instruments of high resolving power, which enabled him to ascertain the duplicity and reversed order of the D-terms of these elements. Beginning with 1927, S. E. Frish published a series of reports devoted to the study of the spark spectrum of sodium. As a result of these studies, the analogy of the spectra NaII and NeI predicted by theory was ascertained and the energy levels of the sodium ion were determined for the first time. In 1930, S. E. Frish conducted measurements of the spark spectrum of neon in the region of 2,200 to 1,500 Å and added an essential contribution to the study of energy levels of NeII. This research turned out to be the beginning of a series of studies dealing with research of spectra in the far ultra-violet range, which S. E. Frish conducted together with V.I.Cherniaev and N.V.Kremenevskii. In the last few years, S.E. Frish turned to the analysis of complex spectra. He studied the spectrum of cerium, conducted research into the magnetic splitting of lines of elements with complex spectra and, together with N. P. Penkin, studied the absorption spectrum of uranium in a King furnace.

S. E. Frish is the most prominent specialist in the systematic of atomic spectra in the (Soviet) Union. His monograph Atomic Spectra, published as early as 1933, serves as a reference book for every spectroscopist.

S. E. Frish's inherent feeling for the new and his ability to pick out the essential problems of research, manifested itself in a new direction of studies, beginning in 1930, and dealing with research into the interaction of an atomic nucleus with an electron shell, leading to the hyperfine structure of spectral lines. These studies enhanced S. E. Frish's reputation in the Soviet Union as well as abroad.

Having studied the structure of the line of ionized sodium, S.E.Frish determined the mechanical moment of a sodium nucleus as I = 3/2, while studies by Schuler and other foreign authors, exploring the reabsorption of the NaI line, did not lead to specific results. S. E. Frish examined the lines of potassium and established an abnormally small value for the magnetic moment of the nucleus of this element. Together with V. A. Matveev, he improved optical instruments and light sources suitable for the study of the hyperfine structure, and together with F. M. Gerasimov established, at the Government Optical Institute, a large diffraction grating. S. E. Frish discovered the abnormally small splitting of several terms of thallium and the strong dependence of the intensity of the components on the excitation conditions and studied the hyperfine structure of lines of silver, calcium, barium and other elements. In 1938, he studied the influence of a nuclear moment on the Zeeman effect in absorption spectra and in 1939, together with M. P. Vaniukov, studied the isotopic shift in lines of samarium. As early as 1934, S. E. Frish realized the advantage in studying the structure of lines of

pure isotopes and, together with V. I. Cherniaev, took steps to enrich hydrogen by deutero-electrolysis and diffusion through palladium. During the post-war years, S. E. Frish expanded his research, on a new basis, on the study of the hyperfine structure of spectra. He posed to his students the problem of studying the spectra of new elements obtained through nuclear reactions. Under the supervision of S. E. Frish, N. I. Kaliteevski and M. P. Chaika conducted research into the hyperfine structure of spectral lines of actinides and established nuclear moments of plutonium and odd isotopes of uranium.

The first research by S. E. Frish in the field of the spectroscopy of a gas discharge and the study of elementary processes in gases took place in 1934. Together with A. A. Ferkhmin and other students, S. E. Frish studied the role of secondary impacts in mixtures of metals. This early work produced interesting data concerning the effective cross-section of secondary impacts, which were defined more accurately by him in 1955, when he studied sensitized fluorescence in a mixture of Na-Hg. From 1938 on, S. E. Frish has been occupied with the solution of a difficult problem concerning the mechanism of the excitation of spectral lines under different discharge conditions, He advanced the idea of the possibility of a spectroscopic study of the directed movement of ions by studying the contours of spectral lines and put it into practice in a series of studies conducted together with his students IU. M. Kagan and V. M. Zakharova, In 1941, S. E. Frish and IU.M.Kagan solved the problem of step excitation of high levels at high current densities in a positive column. The question of the excitation mechanism in negative luminescence was discussed in a study by S.E.Frish and I.P.Bogdanova.

S.E. Frish continued to broaden the arsenal of optical methods which could be utilized to determine the discharge parameters. It appeared that a study of the reabsorption of lines and utilization of the immersion method made it possible to make sufficiently specific deductions concerning the concentration of normal and excited atoms at various levels. Thus, in their studies conducted in 1948, S. E. Frish, N.P. Penkin and A.M. Shukhtin proved the presence of a Boltzmann distribution in a high-temperature oven. The utilization, by students of S.E. Frish, of the classical method of anomalous dispersion in the investigation of a gas discharge made it possible to study a number of its important characteristics. The employment of up-to-date methods of photoelectric recording of spectra permitted S. E. Frish, working together with I.P. Zapesochnyi to study in detail optical excitation functions and to clarify the role played by cascade transitions.

Though being occupied with the development of important theoretical problems of spectroscopy, S. E. Frish always paid attention to its practical applications. As early as 1934, in a study conducted together with V. A. Konovalov, the possibility of analyzing binary mixtures of several gases in a hollow cathode was explained. In 1949, S.E.Frish and E. IA. Schreder developed a method of spectroscopic analysis of gas mixtures with the aid of a high-frequency discharge. In a series of further studies by S.E. Frish together with O.P.Bechkova and others, this method was further developed and a number of important practical problems were solved, of which the method of analyzing micro-quantities of gases, the analysis of complex mixtures, etc., should be mentioned. S.E. Frish's work in this field is widely utilized by industry in the control of processes in the manufacture of pure inert gases.

S. E. Frish always paid close attention to the development and improvement of optical instruments. A lecture course entitled "The Technology of Spectroscopy" published by him in 1936, was for a long time the only manual on this subject in the Soviet Union. S. E. Frish is the inventor of a number of spectral devices, distributed by the Experimental Workshops of the Institute of Physics of the Leningrad State University and used in many laboratories throughout the country. Among these instruments are the following: monochromators for the visible and ultraviolet ranges of the spectrum, a double glass monochromator, a portable quartz spectrograph for geologists (together with A.N.Zaidel'), a spectrograph for the visible range with two Abbe prisms, etc.

The pedagogic activity of S.E. Frish is closely connected with his fruitful scientific work of over 35 years. He has a large number of students and S. E. Frish in fact heads a whole school of spectroscopists. For many years he taught a course in General Physics in the Faculty of Physics of the Leningrad Government University.

Together with A.F. Timoreva, he wrote a three-volume course in physics which continues to be the basic textbook of the faculties of physics and physics-mathematics of all universities in the Soviet Union and those of many VTUZ's (Higher Educational Institutions). This textbook has been translated into Chinese, Czech, Romanian and German. S.E. Frish wrote a large number of scientific-popular articles and pamphlets, disseminating among a wide circle of readers the latest achievement of physics. All his literary efforts are characterized by a strictly systematic presentation, clarity and explicity of statement.

In his work as well as in appearances at philosophic discussions, S.E.Frish always defended the Marxist-Leninist interpretation of the fundamentals of physics against the alien influence of idealists and mechanists. He wrote a series of articles on philosophic questions, in particular he investigated in detail the difficult problem of the interrelation between mass and energy. He actively participates in public life and takes part in educational and organizational work. For many years, S.E. Frish has been one of the directors of the Spectroscopy Commission of the Academy of Sciences of the USSR, and since 1957 he headed the Physics Section of the Educational-Technical Council of the MVO (Ministry of Higher Education) USSR.

S. E. Frish meritoriously represents Soviet science abroad and is a member of the Joint Committee for Spectroscopy at UNESCO.

S. E. Frish meets his 60th year full of energy and creative plans and as head of a large number of students who greatly value his broad erudition and tremendous experience, matched by an exceptionally kind relationship, sensitivity and delicacy.

The editorial staff of Optics and Spectroscopy in the name of all Soviet opticians and spectroscopists congratulate Sergei Eduardovich on his pleasant jubilee and wishes him many years of life and fruitful work.

REGISTRIRUIUSHCHII VAKUUMNYI SPEKTROMETER DLIA DALEKOI INFRAKRASNOI OBLASTI (DIKS-1)

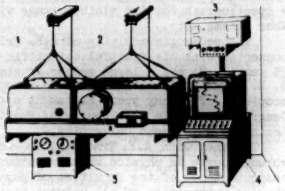
RECORDING VACUUM SPECTROMETER FOR THE FAR INFRARED RANGE (DIKS-1) *

Registriruiushchii vakuumnyi spektrometer DIKS-1 so smennymi diffraktsionnymi reshetkami razmerom 250x250 mm prednaznachen dlia zapisi infrakrasnykh spektrov v oblasti ot 20 do 500 μ (0.5 mm) i bolee s razresheniem do 0.3 cm^{-1}.

Recording vacuum spectrometer DIKS-1 with interchangeable diffraction gratings of 250x250 mm for the tracing of infrared spectra in the 20 - 500 μ (0.5 mm) region and higher and with resolution to 0.3 cm^{-1}.

OBSHCHII VID USTANOVKI SO SPEKTROMETROM DIKS-1

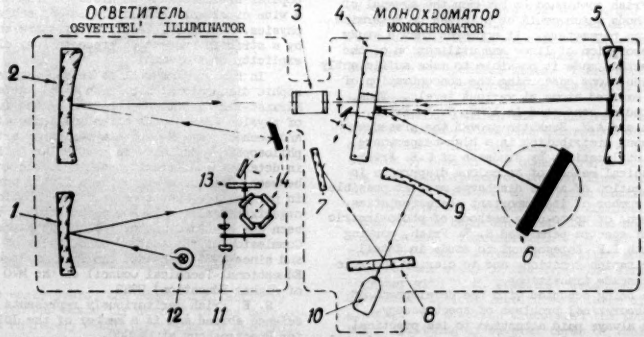
EXTERNAL VIEW OF THE APPARATUS WITH THE DIKS-1 SPECTROMETER



1 - Osvetitel' (Illuminator)
2 - Monokhromator
3 - Usilitel' (Amplifier)
4 - Samopisets (Recorder)
5 - Blok pitaniia s vakuumnoi ustanovkoi (Power supply with vacuum apparatus)

OPTICHESKAIA SKHEMA SPEKTROMETRA DIKS-1

OPTICAL DIAGRAM OF THE DIKS-1 SPECTROMETER



1, 2, 5, 9 - Sfericheskie zerkala (spherical mirrors); 4, 7, 8 - ploskie zerkala (plane mirrors); 3 - gazovaia kiuveta (gas cell); 6 - eshelett (echelette); 10 - priemnik radiatsii (spets. termoelement) [receiver of radiation (detector) (spec. thermocell)]; 11 - ustroistvo dlia polucheniia opornogo napriazheniia sinkhronnogo detektora (apparatus to produce the reference voltage for the synchronous detector); 12 - istochnik dlinnovolnovoi radiatsii (source of longwave radiation); 13 - kristal. moduliator (chopper); 14 - otrazh. fil'try (reflecting filters).

* See page 521 [799]

ABBREVIATIONS OFTEN ENCOUNTERED AND USED HEREIN

DAN USSR	Doklady Akademii Nauk	(Reports of the Academy of Sciences of the USSR)
DAN UkrSSR	Dopovidi Akademii Nauk UkrSSR	(Reports of the Academy of Sciences of the Ukraine SSR)
DAN ArmSSR	Doklady Akademii Nauk ArmSSR	(Reports of the Academy of Sciences of the Armenia SSR)
IAN USSR	Izvestiia Akademii Nauk USSR	(Bulletin of the Academy of Sciences of the USSR)
	SF Seriia fizika	(Physics series)
	SM Seriia matematika	(Mathematics series)
	OKhN Otdelenie khimicheskikh	(Section of chemical sciences)
OiS	Optika i Spektroskopiia	(Optics and Spectroscopy)
PiTE	Pribory i Tekhnika Eksperimenta	(Instruments and Techniques of Experiment)
AE	Atomnaia Energiia	(Atomic Energy)
AZ	Astronomicheskii Zhurnal	(Astronomy Journal)
FMM	Fizika Metallov i Metallovedenie	(Physics of Metals and Metallography)
Radiotekh.	Radiotekhnika	(Radio Engineering)
RiE	Radiotekhnika i Elektronika	(Radio Engineering and Electronics)
UK	Uspekhi Khimii	(Progress in Chemistry)
UFN	Uspekhi Fizicheskikh Nauk	(Progress in Physical Sciences)
UFZ	Ukrainskii Fizichni Zhurnal	(Ukraine Physical Journal)
ZETF	Zhurnal Eksperimental'noi Teoreticheskoi Fiziki	(Journal of Experimental Theoretical Physics - JETP)
ZTF	Zhurnal Tekhnicheskoi Fiziki	(Journal of Technical Physics)
FTT	Fizika Tverkogo Tel	(Solid State Physics)
ZFKh	Zhurnal Fizicheskoi Khimii	(Journal of Physical Chemistry)
ZOKh	Zhurnal Obshchee Khimii	(Journal of General Chemistry
ZNKh	Zhurnal Neorganicheskoi Khimii	(Journal of Inorganic Chemistry)
ZPKh	Zhurnal Prikladnoi Khimii	(Journal of Applied Chemistry)
Tr.	Trudy	(Transactions, as for instance, Tr. FIAN)
FIAN	Fizicheskii Institut Akademii Nauk USSR	(P.N. Lebedev Physical Institut of the Academy of Sciences USSR)
Sb.	Sbornik	(Collection, as for instance, Fizich. sb. L'vovskogo Universitet) Fizich. sb. Fizicheskaia sbornik (Physics Collection)
Uch. Zap.	Uchenye Zapiskii	(Scientific Records)
Vestn.	Vestnik '	(Herald or Messenger)
FTIAN	Fiziko-Tekhnicheskii Institut Akademii Nauk	(Physical-Technical Institute of the Academy of Sciences)
GOI	Gosudarstvennyi Opticheskii Institut	(State Optical Institute)
VEI	Vsesoiuznyi Elektrotechnicheskii Institut	(All-Union Electrotechnical Institute)
MFTI	Moskovskaia Fiziko-Tekhnicheskii Institut	(Moscow Institute of Physics and Technology)
NIIZMIR	Nauchno-Issledovatel'skii Institut Zemnogo Magnetizma, Ionosfery i Rasprostraneniia	(Research Institute of Terrestrial Magnetism and Ionospheric Propagation)
GIFTI	Gor'kovskii Issledovatel'skii Fiziko-Tekhnicheskii Institut	(Gor'kii Research Institute of Physics and Technology)
NIFI	Nauchno-Issledovatel'skii Fizicheskii Institut	(Scientific Research Institute of Physics, Leningrad Univ.)
NIIRFI	Nauchno-Issledovatel'skii Radio-fizicheskii Institut	(Scientific Research Institute of Radiophysics, Gor'kii Univ.)
GITTL	Gostekhizdat - Gosudarstvennoe Izdatel'stvo Tekhniko-Teoreticheskoi Literatury	(State Publishers of Technical-Theoretical Literature)
GIFML	Fizmatgizdat - Gosudarstvennoe Izdatel'stvo Fiziko-Matematicheskoi Literatury	(State Publishers of Physical-Mathematical Literature, formerly Gostekhizdat)
IL or IIL	Izdatel'stvo Inostrannoi Literatury	(Publishers of Foreign Literature)
Izd. AN USSR	Izdatel'stvo Akademiia Nauk USSR	(Academy of Sciences Press)
ZL	Zavodskaia Laboratoriia	(Factory Laboratory)
GOST	Gosudarstvennyi Obshchesoiuznyi Standart	(All - Union State Standard)
LIPAN USSR	Laboratoriia izmeritel'nykh priborov AN USSR	(Laboratory of Measuring Instruments)
IFAN UkrSSR	Institut Fiziki AN UkrSSR, KIEV	(Physics Institute AN Ukr SSR)
SPTI	Sibirskii Fiziko-Tekhnicheskii Institut, Tomsk	(Siberia Physical-Technical Institute)
IFAAN ESSR	Institut Fiziki i Astronomii AN ESSR, Tartu	(Institute of Physics and Astronomy)
IFA AN USSR	Institut fiziki atmosfery AN USSR	(Institute of the Physics of the Atmosphere)

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